OXYGEN CONTAINING COMPOUND

1.0 HYDROXY DERIVATIVES

Hydroxy derivatives → Aliphatic hydroxy derivatives; Aromatic hydroxy derivatives

1.1 Aliphatic Hydroxy Derivatives

Hydroxy derivatives in which —OH is directly attached to sp^3 'C' (Alcoholic compounds).

1.2 Aromatic Hydroxy Derivatives

Hydroxy derivatives in which —OH is directly attached to sp^2 'C' or benzene ring (Phenolic compounds).

Aliphatic hydroxy derivatives :

(a) Classification according to number of —OH groups :

(i) Monohydric [one –OH] $\longrightarrow CH_3CH_2—OH$

(ii) Dihydric [two –OH] $\longrightarrow CH_2(OH)-CH_2(OH)$

(iii) Trihydric [three –OH] $\longrightarrow CH_2(OH)-CH(OH)-CH_2(OH)$

(iv) Polyhydric [n –OH] $\longrightarrow CH_2(OH)-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CH_2(OH)$

(b) Classification according to nature of carbon :

(i) p or 1° – alcohol $\longrightarrow CH_3CH_2 - OH$

(ii) s or 2° – alcohol $\longrightarrow (CH_3)_2CH - OH$

(iii) t or 3° – alcohol $\longrightarrow (CH_3)_3C - OH$

2.0 MONOHYDRIC ALCOHOL

2.1 General Methods of Preparation

(i) From alkanes (By oxidation):

$$(CH_3)_3\,C—H \xrightarrow[\Delta]{H^{\oplus}/KMnO_4} (CH_3)_3\,C—OH$$

(ii) From alkenes :

(a) By hydration :

$$CH_3—CH{=}CH_2 \xrightarrow[H_2O]{H^{\oplus}} CH_3-CH(OH)-CH_3$$

(b) By hydroboration oxidation :

$$CH_3—CH{=}CH_2 \xrightarrow[(2)\,H_2O_2/HO^{\ominus}]{(1)\,BH_3,THF} CH_3-CH_2-CH_2-OH \quad (1^\circ \text{ alcohol})$$

(c) By oxymercuration demercuration :

$$CH_3—CH{=}CH_2 \xrightarrow[(ii)\,NaBH_4]{(i)\,Hg(OAc)_2,H_2O} CH_3-CH(OH)-CH_3$$

(iii) From alkyl halides (By hydrolysis) :

$$CH_3-CH_2-Cl \xrightarrow[\text{or Moist } Ag_2O]{\text{Aq. KOH}} CH_3CH_2-OH$$

(iv) From carbonyl compounds (By reduction) :

$$>C=O \xrightarrow{\text{Reducing agent}} >CH-OH$$

GOLDEN KEY POINTS

Reducing agents may be,

$LiAlH_4/H^{\oplus}$

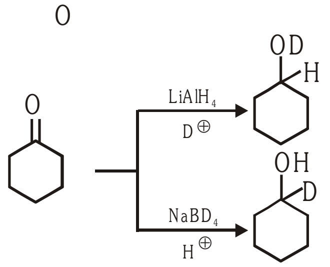
$NaBH_4/H^{\oplus}$

$Na + EtOH$

Ni/H_2

$$R-CHO \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH$$

$$R-\underset{\underset{O}{\|}}{C}-R \xrightarrow[H^{\oplus}]{NaBH_4} R-\underset{\underset{OH}{|}}{CH}-R$$



$$CH_3-CH=CH-CHO \xrightarrow[H^{\oplus}]{LiAlH_4} CH_3-CH=CH-CH_2-OH$$

Crotonaldehyde

(v) From ethers :

$$R-O-R \xrightarrow{dil.H_2SO_4} R-OH + R-OH$$

$$CH_3-O-CH_2CH_3 \xrightarrow{dil.H_2SO_4} CH_3-OH + CH_3CH_2-OH$$

(vi) From acid and derivatives (By reduction) :

$$R-COOH \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH + H_2O$$

$$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH + HCl$$

$$R-\underset{\underset{O}{\|}}{C}-OR \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH + R-OH$$

$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH + R-CH_2-OH$$

Note : Amide on reduction gives amine not alcohol.

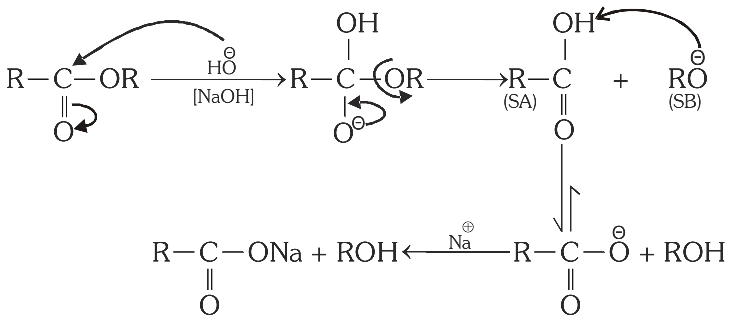
$$R-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-NH_2 + H_2O$$

(vii) From esters (By hydrolysis) :

(a) By alkaline hydrolysis :

$$R-\underset{\underset{O}{\|}}{C}-OR \xrightarrow{NaOH} R-\underset{\underset{O}{\|}}{C}-ONa + R-OH$$

Mechanism :



$$CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow{NaOH} CH_3-\underset{\underset{O}{\|}}{C}-ONa + C_2H_5OH$$

Hydrolysis is Nucleophilic substitution reaction (NSR) and Order of reaction is 2. Alkaline hydrolysis is also called as saponification

$$Ph—COOC_2H_5 \xrightarrow{HO^{\ominus}} Ph—COO^{\ominus} + C_2H_5OH$$

(b) By acidic hydrolysis :

$$R-\underset{\underset{O}{\|}}{C}-OR \underset{H_2O(excess)}{\overset{\overset{\oplus}{H}}{\rightleftharpoons}} R-\underset{\underset{O}{\|}}{C}-OH + R-OH$$

$$CH_3-\underset{\underset{O}{\|}}{C}-\overset{18}{O}C_2H_5 \overset{H_3\overset{\oplus}{O}}{\rightleftharpoons} CH_3-\underset{\underset{O}{\|}}{C}-OH + C_2H_5\overset{18}{O}H$$

(viii) From p-amines :

$$R—NH_2 \xrightarrow[\text{or } HNO_2]{NaNO_2+HCl(aq.)} R—OH + N_2$$

$$CH_3CH_2—NH_2 \xrightarrow{HNO_2} CH_3CH_2—OH + N_2$$

Mechanism :

$$CH_3CH_2-NH_2 \xrightarrow{NaNO_2+HCl} \underset{\text{(Unstable)}}{CH_3CH_2-\overset{\oplus}{N_2}\overset{\ominus}{Cl}} \longrightarrow CH_3\overset{\oplus}{C}H_2 + N_2 + \overset{\ominus}{Cl}$$

$$CH_3\overset{\oplus}{C}H_2 \xrightarrow{H_2O} CH_3CH_2-OH \text{ [major]}$$

$$CH_3\overset{\oplus}{C}H_2 \xrightarrow{\overset{\ominus}{Cl}} CH_3CH_2-Cl$$

$$CH_3\overset{\oplus}{C}H_2 \xrightarrow{\overset{\ominus}{\ddot{O}}-N=O} CH_3CH_2-O-N=O + CH_3-CH_2-NO_2$$

$$CH_3\overset{\oplus}{C}H_2 \xrightarrow{-\overset{\oplus}{H}} CH_2=CH_2$$

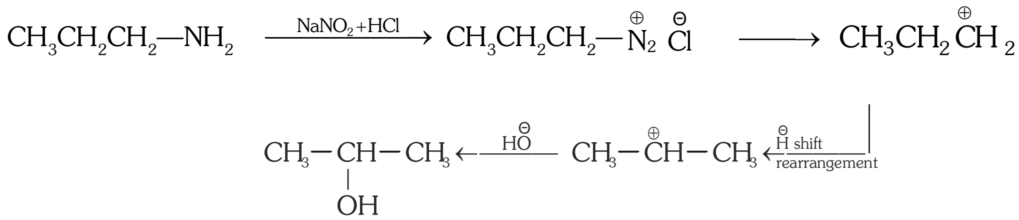
$$CH_3\overset{\oplus}{C}H_2 \xrightarrow{CH_3-CH_2-OH} CH_3-CH_2-O-CH_2-CH_3$$

(side products)

Intermediate is carbocation so rearrangement may be possible.

Illustration 1. $CH_3CH_2CH_2—NH_2 \xrightarrow{NaNO_2+HCl} ?$

Solution. **Mechanism :**



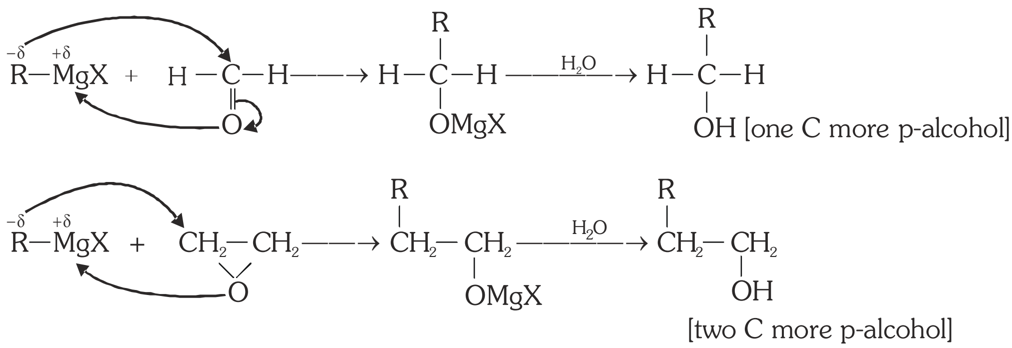
Exception : $CH_3 — NH_2 \xrightarrow{HNO_2} CH_3 — O — CH_3$

(ix) From Grignard reagent :

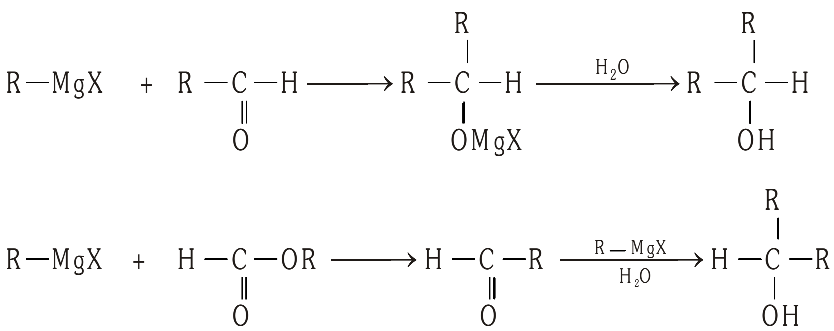
(a) p-alcohol :

$R—MgX + [O] \longrightarrow R—O—MgX \xrightarrow{H_2O} R—OH$

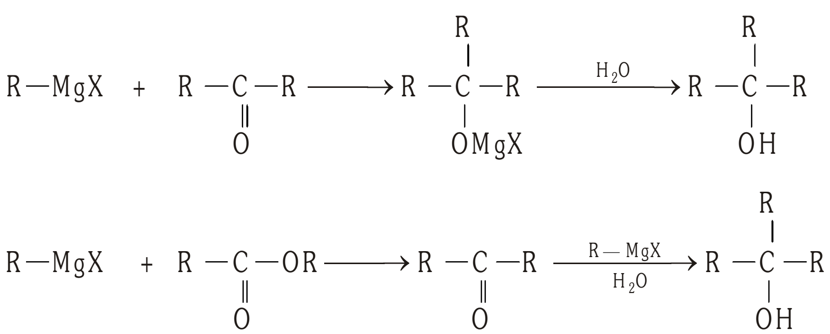
[Same C-p-alcohol]



(b) s-alcohol :



(c) t-alcohol :



Physical properties :

(i) C_1 to C_{11} are colourless liquids and higher alcohols are solids.

(ii) Density of monohydric alcohol is less than H_2O.

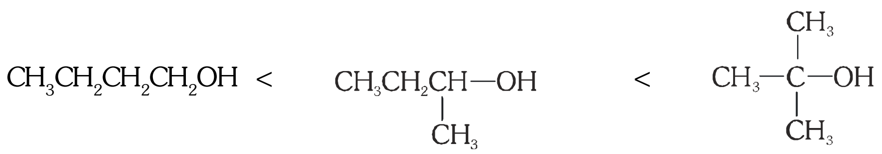
(iii) Density ∝ mol. wt. (for monohydric alcohol).

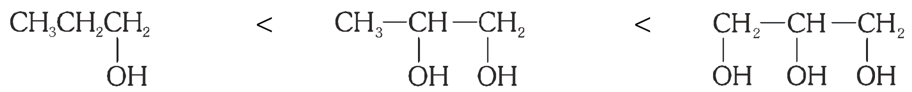
(iv) **Solubility :** C_1 to C_3 and t-butyl alcohol is completely soluble in H_2O due to H–bonding.

$$\text{solubility} \propto \frac{\text{No. of side chains}}{\text{molecular weight}}$$

Order of solubility :

C_4H_9OH > $C_5H_{11}OH$ > $C_6H_{13}OH$

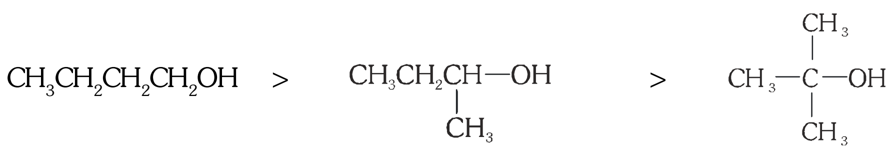


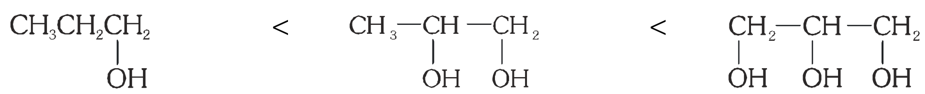


[Number of OH increases, H-bonding increases]

(v) **Boiling points :** $$BP \propto \frac{\text{molecular weight}}{\text{No. of side chains}}$$

Orber of BP : C_4H_9OH < $C_5H_{11}OH$ < $C_6H_{13}OH$





[Number of OH increases, H-bonding increases]

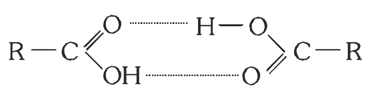
Illustrations

Illustration 2. Boiling point of alcohol is more than corresponding ether. Why ?

Solution. H-bonding in alcohol.

Illustration 3. Boiling point of alcohol is less than corresponding carboxylic acid. Why ?

Solution. Dimer formation in carboxylic acid.



2.3 Chemical Properties

Monohydric alcohol shows following reactions

(A) Reaction involving cleavage of O ┼ H

(B) Reaction involving cleavage of C ┼ OH

(C) Reaction involving complete molecule of alcohol

(A) Reaction involving cleavage of O $+$ H : Reactivity order (Acidic nature) is

$CH_3—OH \quad > \quad CH_3CH_2—OH \quad > \quad (CH_3)_2CH—OH \quad > \quad (CH_3)_3C—OH$

(i) Acidic nature :

$H_2O > R—OH > CH\equiv CH > NH_3$ (Acidic strength)

Alcohols are less acidic than H_2O and neutral for litmus paper and give H_2 with active metals (Na, K)

$$R—OH + Na \longrightarrow R—ONa + \frac{1}{2}H_2$$

$$R—OH + K \longrightarrow R—OK + \frac{1}{2}H_2$$

(ii) Alkylation:

$$R—OH \xrightarrow{CH_2N_2/\Delta} R—O—CH_2—H$$

$$R—OH \xrightarrow{Na} R—ONa \xrightarrow{R-X} R—O—R$$

(Williamson synthesis)

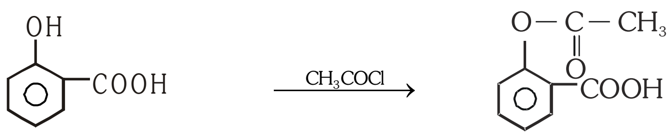
(iii) Acylation :

$$R-OH + Cl-\underset{\underset{O}{\|}}{C}-R \longrightarrow R-O-\underset{\underset{O}{\|}}{C}-R$$

(Acylation)

$$R-OH + Cl-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow R-O-\underset{\underset{O}{\|}}{C}-CH_3$$

(Acetylation)



Salicylic acid

Acetoxy benzoic acid

Acetyl salicylic acid

Aspirin [Used as analgesic and antipyretic]

(iv) Benzoylation : (Schotten Baumann's Reaction) :

$$R-OH + Cl-\underset{\underset{O}{\|}}{C}-Ph \longrightarrow R-O-\underset{\underset{O}{\|}}{C}-Ph$$

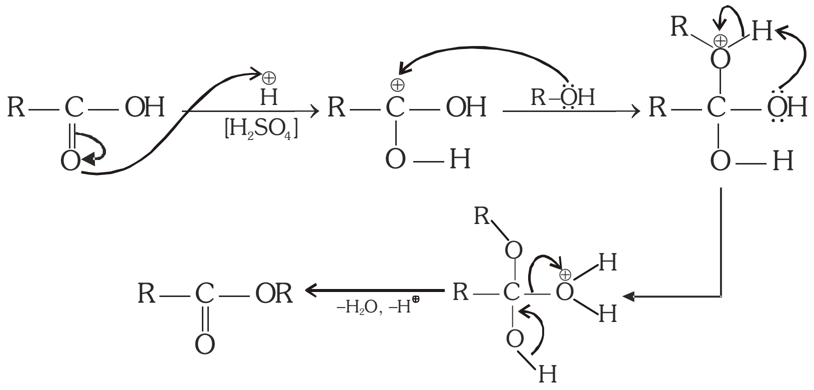
(Benzoylation)

(v) Esterification :

$$R-\underset{\underset{O}{\|}}{C}-OH + R-OH \xrightarrow[\Delta]{conc.\ H_2SO_4} R-\underset{\underset{O}{\|}}{C}-OR + H_2O$$

Conc. H_2SO_4 is used as catalyst and dehydrating agent.

Mechanism :



Ex. $CH_3-\underset{\underset{O}{\|}}{C}-\boxed{OH + H}-OC_2H_5 \xrightarrow[\Delta]{\text{conc. } H_2SO_4} CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + H_2O$

Ex. $Ph-\underset{\underset{O}{\|}}{C}-\boxed{OH + H}-\overset{18}{O}C_2H_5 \xrightarrow{\text{conc. } H_2SO_4} Ph-\underset{\underset{O}{\|}}{C}-\overset{18}{O}C_2H_5 + H_2O$

Dry HCl can also be used as dehydrating agent.

Ex. $CH_3-\underset{\underset{O}{\|}}{C}-\boxed{OH + H}-OC_2H_5 \xrightarrow[\Delta]{\text{dry HCl}} CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + H_2O$

GOLDEN KEY POINTS

- Reactivity for esterification $\propto \dfrac{1}{\text{Steric hindrance}}$.
- Reactivity of R – OH [If acid is same] : $CH_3-OH > 1° > 2° > 3°$ alcohol
- Reactivity of RCOOH [If alcohol is same] :

$$H-\underset{\underset{O}{\|}}{C}-OH > CH_3-\underset{\underset{O}{\|}}{C}-OH > CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OH > CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{O}{\|}}{C}-OH$$

(vi) Reaction with CH≡CH :

$$CH\equiv CH + 2CH_3-OH \xrightarrow[\Delta]{BF_3/HgO} CH_3CH\begin{matrix} OCH_3 \\ OCH_3 \end{matrix}$$

Methylal

$$CH\equiv CH + 2CH_3CH_2-OH \xrightarrow[\Delta]{BF_3/HgO} CH_3CH\begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix}$$

Ethylal

(vii) Reaction with carbonyl compounds :

$$R{-}CHO + 2R{-}OH \xrightarrow{H^{\oplus}} R-CH\begin{smallmatrix} OR \\ OR \end{smallmatrix}$$

Acetal

$$R-\underset{\underset{O}{\|}}{C}-R + 2R-OH \xrightarrow{H^{\oplus}} \begin{smallmatrix} R \\ R \end{smallmatrix}{>}C{<}\begin{smallmatrix} OR \\ OR \end{smallmatrix}$$

Ketal

$$CH_3CHO + 2CH_3{-}OH \xrightarrow{H^{\oplus}} CH_3CH\begin{smallmatrix} OCH_3 \\ OCH_3 \end{smallmatrix}$$

Methylal

(viii) Reaction with Grignard reagent :

$$R{-}MgX + H{-}OR \longrightarrow R-H + Mg\begin{smallmatrix} X \\ OR \end{smallmatrix}$$

(B) Reaction involving cleavage of C┼OH : Reactivity order or basic nature is

$CH_3{-}OH$ < $CH_3CH_2{-}OH$ < $(CH_3)_2CH{-}OH$ < $(CH_3)_3C{-}OH$

(i) Reaction with halogen acid :

$$R{-}CH_2{-}OH + HCl \xrightarrow[\Delta]{ZnCl_2} R{-}CH_2{-}Cl + H_2O$$

Reactivity order of the acids is HI > HBr > HCl

(ii) Reaction with phosphorous halides :

$$3R{-}OH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

$$R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$$

(iii) Reaction with thionyl chloride ($SOCl_2$) :

$$R{-}OH + SOCl_2 \xrightarrow{\text{Pyridine}} R{-}Cl + \underset{\text{(gas)}}{SO_2\uparrow} + HCl$$

(iv) Reaction with NH_3 : Alumina (Al_2O_3) is used as dehydrating agent.

$$R\boxed{-OH + H}NH_2 \xrightarrow[250^\circ C]{Al_2O_3} R{-}NH_2 + H_2O$$

(C) Reaction involving complete molecule of alcohol :

(i) Dehydration : Removal of H_2O

(a) Intermolecularly removal of H_2O [formation of ether]

(b) Intramolecularly removal of H_2O [formation of alkene]

$$\underset{\text{(conc.)}}{C_2H_5{-}OH + H_2SO_4} \begin{cases} \xrightarrow{140^\circ C} C_2H_5{-}O{-}C_2H_5 \text{ (Williamson's continuous etherification)} \\ \xrightarrow{170^\circ C} CH_2{=}CH_2 \text{(Elimination)} \end{cases}$$

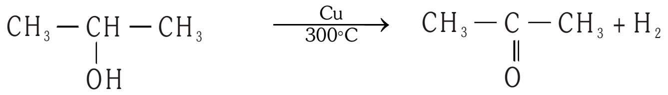
$$C_2H_5OH + \underset{\text{(Alumina)}}{Al_2O_3} \begin{cases} \xrightarrow{250^\circ C} C_2H_5{-}O{-}C_2H_5 \\ \xrightarrow{350^\circ C} CH_2{=}CH_2 \end{cases}$$

Ease of dehydration follows the order : **3° ROH > 2° ROH > 1° ROH**

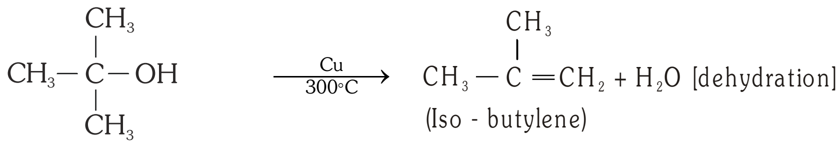
(ii) Catalytic Dehydrogenation :

$$CH_3CH_2OH \xrightarrow[300^\circ C]{Cu} CH_3CHO + H_2$$

(p- alcohol) (Acetaldehyde)



(s- alcohol) (acetone)

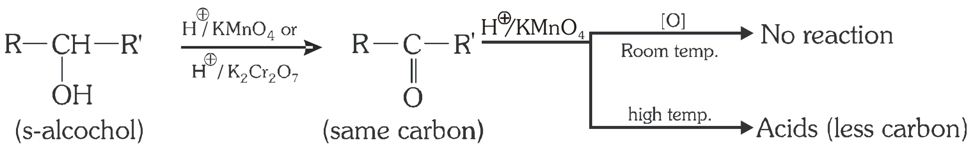


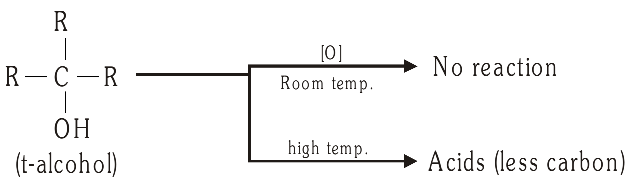
(t–alcohol) (Iso - butylene)

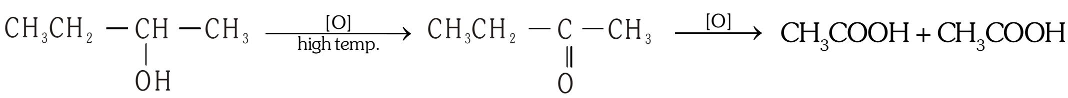
(iii) Oxidation :

$$R\text{—}CH_2\text{—}OH \xrightarrow[H^\oplus/K_2Cr_2O_7]{H^\oplus/KMnO_4 \text{ or}} RCHO \xrightarrow[\text{Room temp.}]{[O]} RCOOH$$

(p-alcohol) (same carbon acid)







Carbonyl group goes with smaller alkyl group [Popoff's rule suggested for oxidation of unsymmetrical ketones]

(iv) Distinction between 1°, 2° and 3° alcohols :

(a) Lucas test : A mixture of HCl(conc.) and anhydrous $ZnCl_2$ is called Lucas reagent.

p-alcohol $\xrightarrow{ZnCl_2+HCl}$ No turbidity at room temp. [On heating within 30 minutes.]

s-alcohol $\xrightarrow{ZnCl_2+HCl}$ Turbidity appears within 5 minutes.

t-alcohol $\xrightarrow{ZnCl_2+HCl}$ Turbidity appears within 2-3 sec.

(b) Victor - Meyer test :

p-alcohol $\longrightarrow$ Red colour

s-alcohol $\longrightarrow$ Blue colour

t-alcohol $\longrightarrow$ No colour

$$R-CH_2-OH\ [1^\circ] \xrightarrow{P + I_2} R-CH_2-I \xrightarrow{AgNO_2} RCH_2-NO_2 \xrightarrow{HNO_2} \underset{\text{Nitrolic acid (blue)}}{R-\underset{\underset{N-OH}{\|}}{C}-NO_2} \xrightarrow{NaOH} \text{Sodium nitrolate (Red)}$$

$$R_2CH-OH\ [2^\circ] \xrightarrow{P + I_2} R_2CH-I \xrightarrow{AgNO_2} R_2CH-NO_2 \xrightarrow{HNO_2} \underset{\text{Pseudonitrol (blue)}}{R_2\underset{\underset{N=O}{|}}{C}-NO_2} \xrightarrow{NaOH} \text{No reaction (Remains blue)}$$

$$R_3C-OH\ [3^\circ] \xrightarrow{P + I_2} R_3C-I \xrightarrow{AgNO_2} R_3C-NO_2 \xrightarrow{HNO_2} \underset{\text{Colourless}}{\text{No reaction}}$$

(C) Dichromate test :

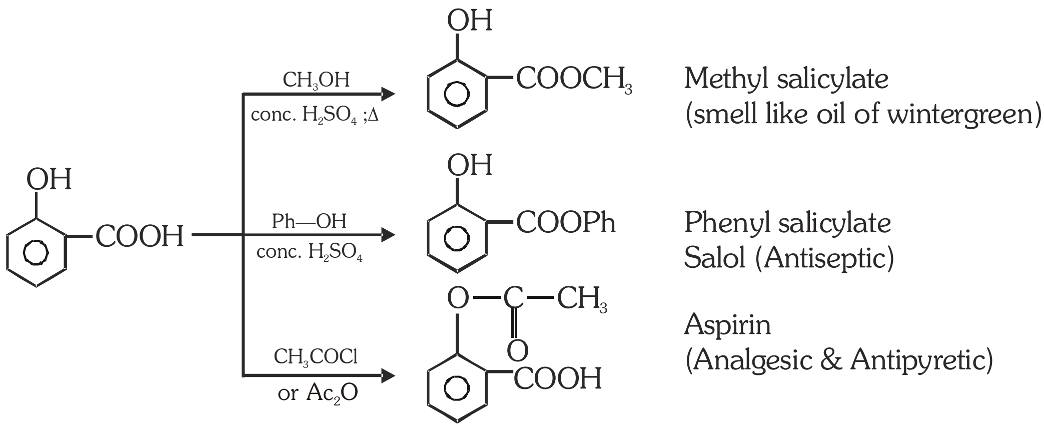
$$1^\circ \text{ Alcohol} \xrightarrow[\text{orange }[Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7} \text{Acid} + \underset{[\text{green}]}{Cr^{+3}}$$

$$2^\circ \text{ Alcohol} \xrightarrow[\text{orange }[Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7} \text{Ketone} + \underset{[\text{green}]}{Cr^{+3}}$$

$$3^\circ \text{ Alcohol} \xrightarrow[\text{orange }[Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7} \text{No oxidation, Remains orange}$$

(v) Distinction between CH_3-OH and C_2H_5OH

	CH_3OH	CH_3CH_2OH
B.P.	65℃	78℃
I_2 + NaOH	No ppt	Yellow ppt of CHI_3
Cu/300℃	Smell of formalin [HCHO]	No smell
Salicylic acid	Smell like oil of wintergreen	No smell



BEGINNER'S BOX-1

1. Which of the following reactions of alkanols does not involve C–O bond breaking

(1) $CH_3CH_2OH + SOCl_2$ (2) $CH_3CH(OH)CH_3 + PBr_3$

(3) $CH_3CH_2OH + CH_3COOH$ (4) $ROH + HX$

2. Which of the folowing alkanols is most soluble in water

(1) 1–Butanol (2) 2–Butanol (3) Isobutyl alcohol (4) t–Butyl alcohol

3. $CH_3CH_2CH_2\text{–}OH \xrightarrow{PCl_5} A \xrightarrow{Alc.KOH} B \xrightarrow{H_3O^{\oplus}} C$

Find product 'C' is

(1) $CH_3CH{=}CH_2$ (2) $CH_3\text{–}\underset{\substack{|\\ OH}}{CH}\text{–}CH_3$ (3) $CH_3\text{–}\underset{\substack{|\\ Cl}}{CH}\text{–}CH_3$ (4) $CH_3CH_2CH_2\text{–}Cl$

Important facts about alcohols

(i) Toxicity [ethyl alcohol < Iso propyl alcohol < methyl alcohol]

(ii) Absolute alcohol : Ethyl alcohol - 99.5%-100%

(iii) Power alcohol : Rectified spirit + C_6H_6 + Petrol for generation of power

(iv) Methylated spirit : Methanol + Pyridine + mineral naptha + rectified spirit.

(v) 70% CH_3OH is known as wood spirit.

(vi) 90% C_2H_5OH is known as Raw spirit.

(vii) C_2H_5OH is technically called WASH.

(viii) Rectified spirit contains 95.5% alcohol and 4.5% H_2O.

GOLDEN KEY POINTS

Oxidation by HIO_4 [per iodic acid] or $(CH_3COO)_4Pb$ [lead tetraacetate] :

$$\underset{\substack{|\\ OH}}{CH_2}\,\vdots\,\underset{\substack{|\\ OH}}{CH_2} \xrightarrow{HIO_4} HCHO + HCHO$$

(Ethylene glycol)

$$\underset{\substack{|\\ OH}}{CH_2}\,\vdots\,\underset{\substack{|\\ OH}}{CH}\,\vdots\,\underset{\substack{|\\ OH}}{CH_2} \xrightarrow{HIO_4} HCHO+HCOOH+HCHO$$

Glycerol

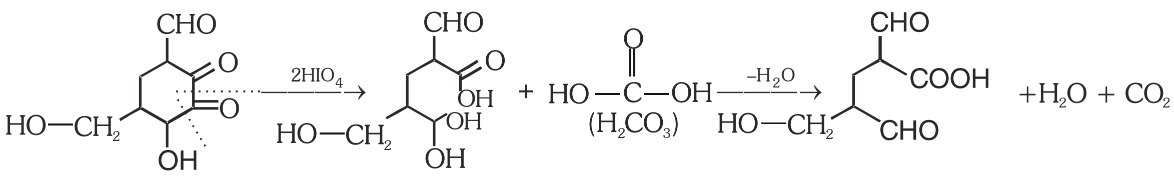
Condition for oxidation by HIO_4 or $(CH_3COO)_4Pb$

(i) At least 2 —OH or 2 >C=O or 1 —OH and 1 >C=O should be at vicinal carbons.

(ii) One HIO_4 breaks one C–C bond and adds one –OH to each carbon .

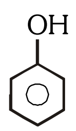
Ex. $CH_3-\underset{OH}{CH}-\underset{OH}{CH}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow{2HIO_4} \left[CH_3-\underset{OH}{CH}-OH + \overset{OH}{\underset{OH}{CH}}-OH + HO-\overset{CH_3}{\underset{OH}{C}}-CH_3\right] \xrightarrow{-3H_2O} CH_3CHO + HCOOH + CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

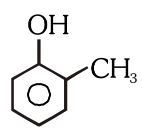
Ex. $CH_3-\underset{O}{\underset{\|}{C}}-\underset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{1HIO_4} \left[CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-\underset{OH}{CH}CH_2-\overset{O}{\overset{\|}{C}}-H\right] \xrightarrow{-H_2O} CH_3COOH + CHO-CH_2-CHO$

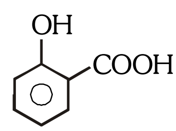
Ex. 

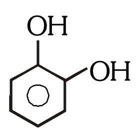
4.0 AROMATIC HYDROXY DERIVATIVES

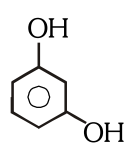
Phenolic compounds : Compounds in which —OH group is directly attached to sp^2c [Benzene ring]

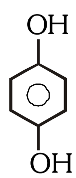

Phenol


o-Cresol


Salicylic acid


Catechol


Resorcinol


Quinol

All phenolic compounds give colour with neutral $FeCl_3$.

$Ph-OH \xrightarrow{\text{neutral } FeCl_3}$ Violet colour

$CH_3CH_2-OH \xrightarrow{\text{neutral } FeCl_3}$ No colour

PHENOL (C_6H_5OH)

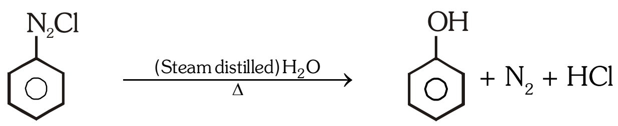
Phenol is also known as carbolic acid. In phenol —OH group is attached with sp^2 hybridised carbon.

4.1 General Methods of Preparation

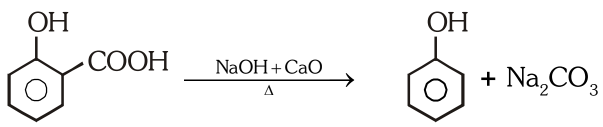
(1) From benzene sulphonic acid : When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.

$$C_6H_5SO_3Na \xrightarrow[(2)\ H^{\oplus}]{(1)\ NaOH, \Delta \ \& \ Pr.} C_6H_5OH + Na_2SO_3$$

(2) From benzene diazonium chloride : When benzene diazonium chloride solution is warmed with water, phenol is obtained with evolution of nitrogen.



(3) By distilling a phenolic acid with sodalime (decarboxylation):

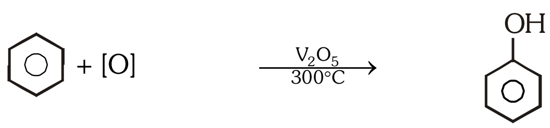


Salicylic acid

(4) From Grignard reagent : The Grignard reagent on reaction with oxygen and subsequent hydrolysis yields phenol.

$$C_6H_5MgBr \xrightarrow{[O]} C_6H_5OMgBr \xrightarrow{H_2O} C_6H_5OH + Mg\begin{matrix} Br \\ OH \end{matrix}$$

(5) From benzene :



(6) From chloro benzene :

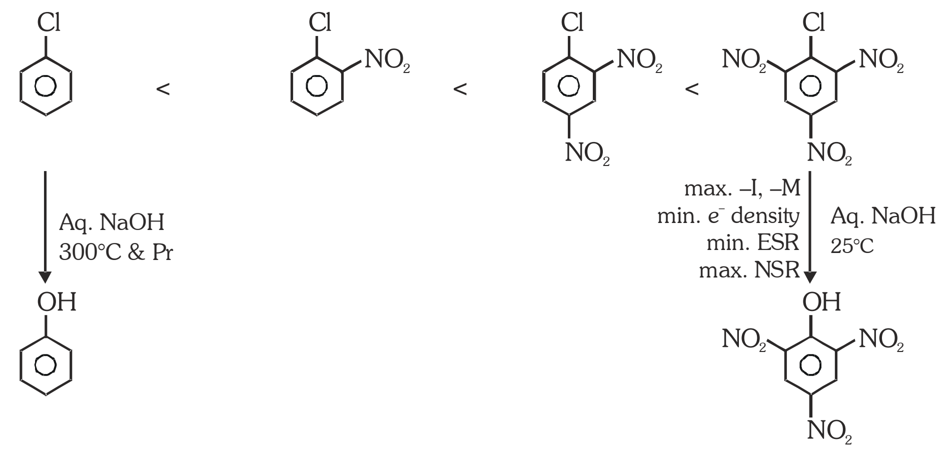
$$Ph—Cl \xrightarrow{Aq.\ NaOH} \text{No NSR at normal condition}$$

Stable by resonance

$$R—Cl \xrightarrow{Aq.\ NaOH} R—OH\ [NSR]$$

$$Ph—Cl \xrightarrow[(2)\ H^{\oplus}]{(1)\ Aq.\ NaOH,\ \Delta \ \& \ Pr} Ph—OH\ [\text{NSR at high temperature}]$$

Order for NSR :



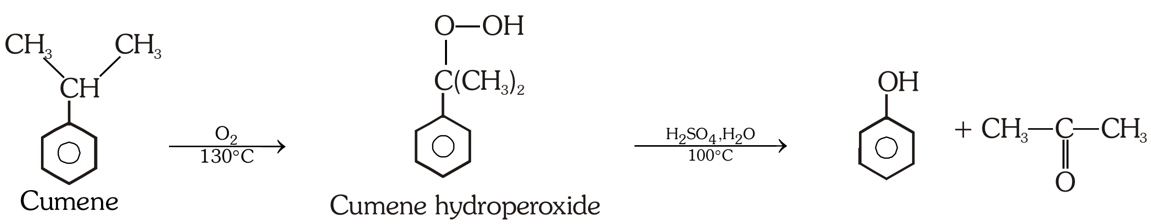
2, 4, 6–Trinitrophenol (Picric acid)

(7) Industrial preparation of phenol: Phenol can be prepared commercially by **:**

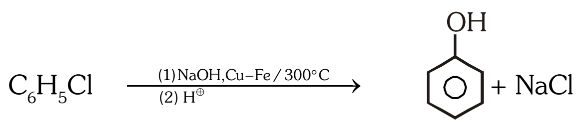
(a) Cumene

(b) Dow's process

(a) From cumene (Isopropyl benzene) : Cumene is oxidised with oxygen into cumene hydroperoxide in presence of a catalyst. This is decomposed by dil. H_2SO_4 into phenol and acetone.

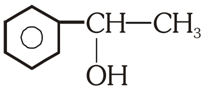
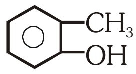


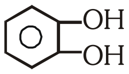
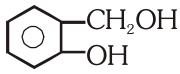
(b) Dow process : This process involves alkaline hydrolysis of chloro benzene-(obtained by above process) followed by acidification.



BEGINNER'S BOX-2

1. Which of the following compounds does not show phenolic properties :-

(1) 
(2) 

(3) 
(4) 

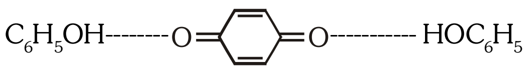
2. The number of dihydric phenols possible with the molecular formula $C_6H_6O_2$ is :-

(1) 2 (2) 3 (3) 4 (4) 5

4.2 Physical Properties

(i) Phenol is a colourless, crystalline solid.

(ii) It attains pink colour on exposure to air and light. (slow oxidation)



Phenoquinone(pink colour)

(iii) It is poisonous in nature but acts as antiseptic and disinfectant.

(iv) Phenol is slightly soluble in water, readily soluble in organic solvents.

(v) Solublity of phenol in water is much lower than alcohols because of larger hydrocarbon part in the molecule.

(vi) Due to intermolecular H-Bonding, phenol has relatively high boiling point than the corresponding hydrocarbons, aryl halides.

4.3 Chemical Properties

(A) Reactions due to –OH group :

(i) Acidic Nature : Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution. The phenoxide ion is stable due to resonance. The negative charge is spread through out the benzene ring which is stabilising factor in the phenoxide ion. Electron withdrawing groups ($-NO_2$, $-Cl$) increase the acidity of phenol while electron releasing groups ($-CH_3$ etc.) decrease the acidity of phenol.

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5\overset{\ominus}{O} + H_3\overset{\oplus}{O}$$

Phenol is stronger acid than alcohols but weaker than the carboxylic acids and even carbonic acid.

GOLDEN KEY POINTS

- The acidic nature of phenol is observed as the following:

(i) Phenol changes blue litmus to red.

(ii) Highly electro positive metals react with phenol.

$$2C_6H_5OH + 2Na \longrightarrow 2C_6H_5ONa + H_2$$

(iii) Phenol reacts with strong alkalies to form phenoxides.

$$C_6H_5OH + NaOH \longrightarrow C_6H_5\overset{\ominus}{O}\overset{\oplus}{N}a + H_2O$$

(iv) However phenol does not decompose Na_2CO_3 or $NaHCO_3$ because phenol is weaker acid than carbonic acid.

$$C_6H_5OH + Na_2CO_3 \text{ or } NaHCO_3 \longrightarrow \text{No reaction}$$

Ph—OH	+	$NaHCO_3$	$\leftrightharpoons$	Ph—ONa	+	H_2CO_3
Acid-I		Base-I		Base-II		Acid-II

$$\left.\begin{array}{lll} \text{Acid-I} & < & \text{Acid-II} \\ \text{Base-I} & < & \text{Base-II} \end{array}\right\} \text{Reaction in reverse direction.}$$

Note : Acetic acid reacts with $NaHCO_3$ and gives effervescence of CO_2.

$$CH_3-\underset{\underset{O}{\|}}{C}-OH + NaHCO_3 \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-ONa + H_2CO_3 \quad [H_2O + CO_2\uparrow]$$

Acid-I	Base-I	Base-II	Acid-II

$$\left.\begin{array}{lll} \text{Acid-I} & > & \text{Acid-II} \\ \text{Base-I} & > & \text{Base-II} \end{array}\right\} \text{Reaction in forward direction.}$$

(ii) Reaction with PCl_5 : Phenol reacts with PCl_5 to form chloro benzene. $POCl_3$ formed as biproduct reacts with phenol to form triphenyl phosphate.

$$C_6H_5OH + PCl_5 \xrightarrow{\Delta} C_6H_5Cl + POCl_3 + HCl$$

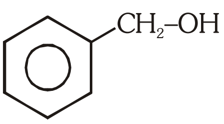
$$3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$$

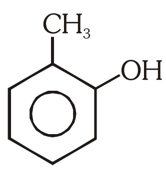
(iii) Reaction with Zn dust: When phenol is distilled with zinc dust benzene is obtained.

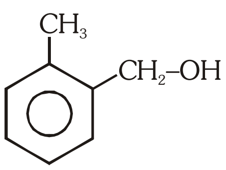
$$C_6H_5OH + Zn \xrightarrow{\Delta} C_6H_6 + ZnO$$

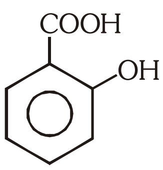
Illustrations

Illustration 4. In which of the following compound deoxygenation is possible when heated with Zn

(I) 

(II) 

(III) 

(IV) 

(1) I, II, III (2) I, III, IV (3) II, IV (4) II, III

Solution **Ans.(3)** Observed in phenolic compound.

(iv) Reaction with NH_3(Bucherer reaction): Phenol reacts with NH_3 in presence of anhydrous $ZnCl_2$ to form aniline.

$$C_6H_5OH + NH_3 \xrightarrow[300°C]{\text{Anhydrous } ZnCl_2 \text{ or } (NH_4)_2SO_3/NH_3 150°C} C_6H_5NH_2 + H_2O$$

(v) Reaction with $FeCl_3$: Phenol gives violet colouration with $FeCl_3$ solution (neutral) due to formation of a complex.

$$C_6H_5OH + FeCl_3 \longrightarrow \text{Violet colour}$$

This reaction is used to differentiate phenol from alcohols.

(vi) Acetylation : Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.

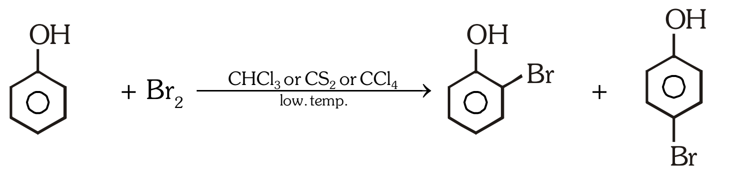
$$C_6H_5OH + ClCOCH_3 \xrightarrow[-HCl]{NaOH} C_6H_5O-\underset{\underset{O}{\|}}{C}-CH_3$$

(vii) Benzoylation (Schotten-Baumann reaction)

$$C_6H_5OH + Cl-\underset{\underset{O}{\|}}{C}-C_6H_5 \xrightarrow[-HCl]{NaOH} C_6H_5O-\underset{\underset{O}{\|}}{C}-C_6H_5$$

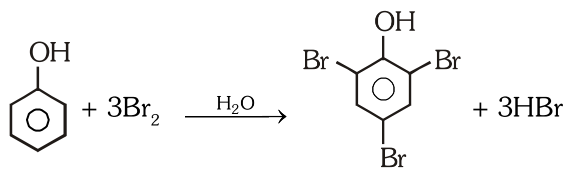
(B) Reaction of Benzene Ring : The —OH group is ortho and para directing. It activates the benzene nucleus.

(i) Halogenation : Phenol reacts with bromine in CCl_4 to form mixture of o–and p–bromo phenol.

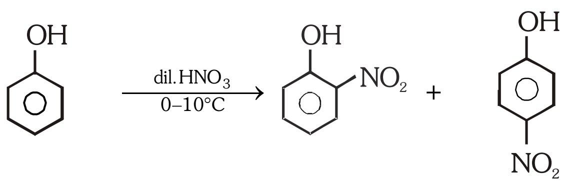


(Major)

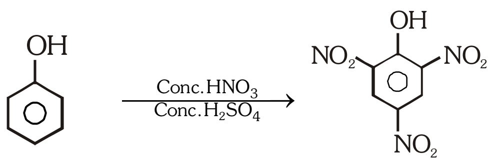
Phenol reacts with bromine water to form a white ppt. of 2,4,6-tribromo phenol. (Test for phenol)



(ii) Nitration : Phenol reacts with dil. HNO_3 at 0°–10°C to form o- and p- nitro phenols.

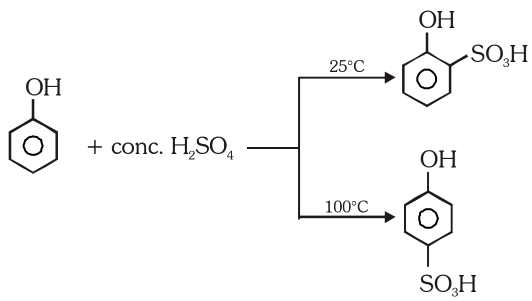


When phenol is treated with nitrating mixture it forms 2,4,6- trinitro phenol (picric acid) but it is not good method to form picric acid because nitric acid oxidise phenol into p-Bezoquinone

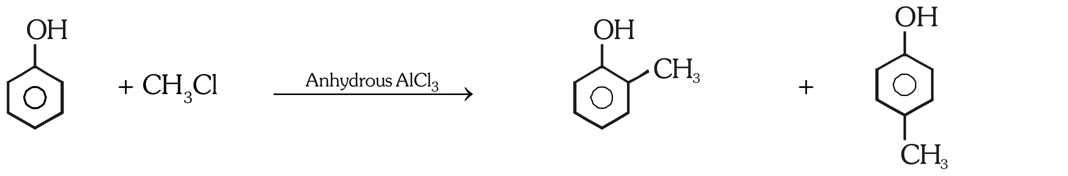


[2, 4, 6–Trinitrophenol (Picric acid)]

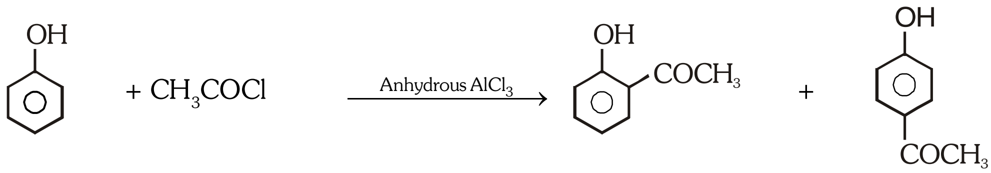
(iii) Sulphonation: Phenol reacts with fuming H_2SO_4 to form o–and p–hydroxy benzene sulphonic acid at different temperatures.



(iv) Friedel - Craft 's reaction:



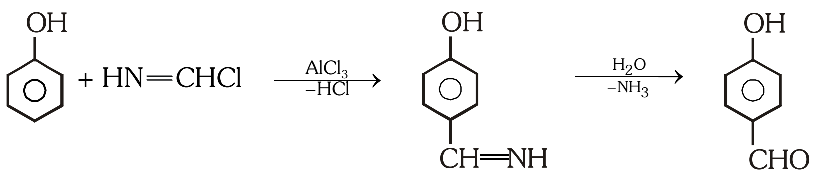
o – cresol p – cresol (Major)



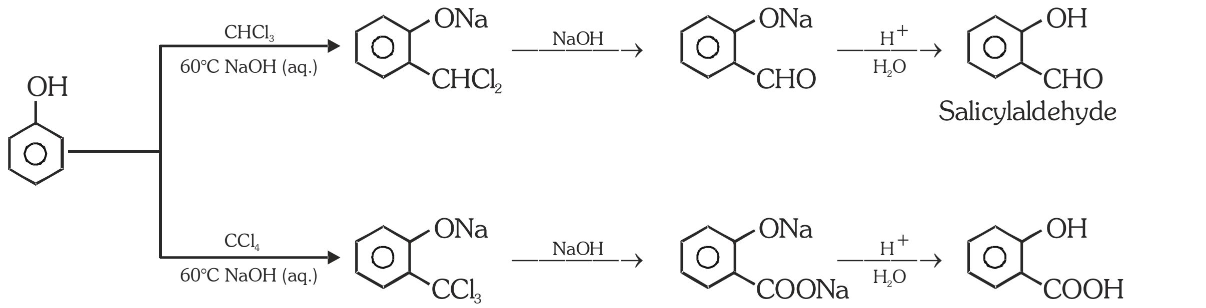
o – and p – hydroxy acetophenone

(v) Gattermann aldehyde synthesis : When phenol is treated with liquid HCN and HCl gas in presence of anhydrous $AlCl_3$ it yields mainly p- hydroxy benzaldehyde (formylation)

$$HCl + HCN \xrightarrow{AlCl_3} HN{=}CHCl$$

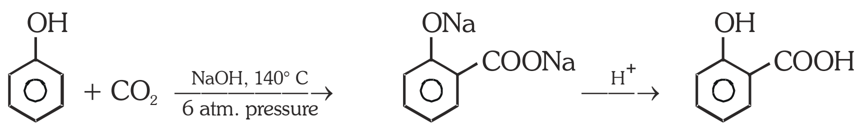


(vi) Reimer-Tiemann reaction : Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o–hydroxy benzaldehyde. When CCl_4 is used salicylic acid is formed.



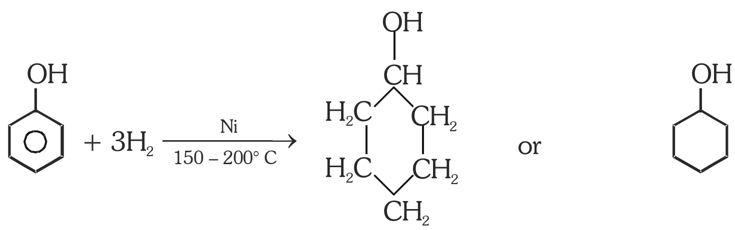
Salicylic acid

(vii) Kolbe's Schmidt reaction : It involves the reaction of C_6H_5OH with CO_2 and NaOH at 140°C followed by acidification to form salicylic acid.



Sodium salicylate Salicylic acid

(viii) Hydrogenation: Phenol when hydrogenated in presence of Ni at 150-200°C forms cyclohexanol.



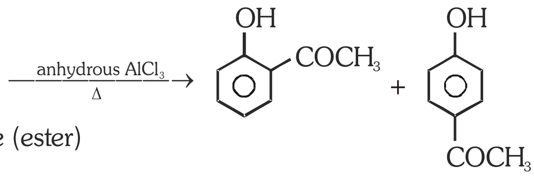
Cyclohexanol. ($C_6H_{11}OH$) (used as a good solvent)

(ix) Fries rearrangement reaction:

$$C_6H_5OH + CH_3COCl \xrightarrow{\text{Pyridine}} C_6H_5OCOCH_3$$

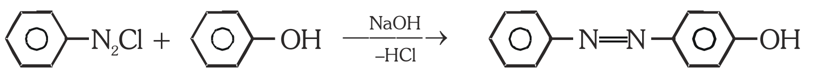
Phenyl Acetate

$C_6H_5OCOCH_3$



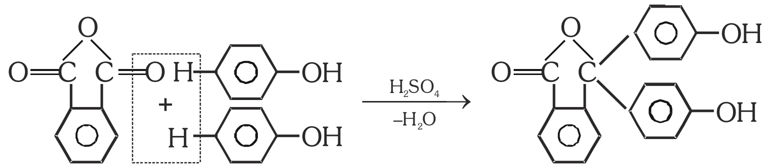
Phenyl acetate (ester)

(x) Coupling reactions: Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a dye (p- hydroxy azobenzene) orange dye.



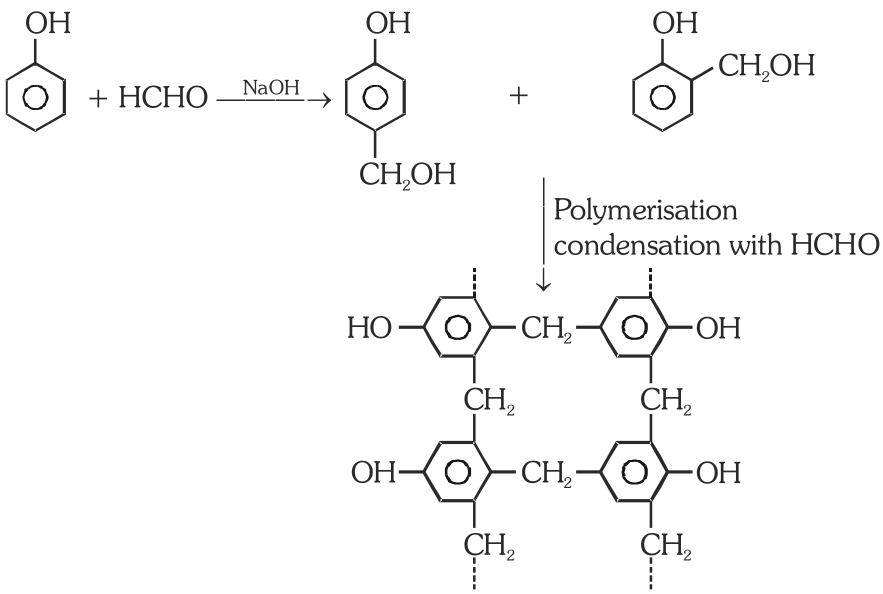
p–hydroxy azobenzene (Orange dye)

Phenol couples with phthalic anhydride in presence of conc. H_2SO_4 to form a dye (phenolphthalein) used as an indicator.



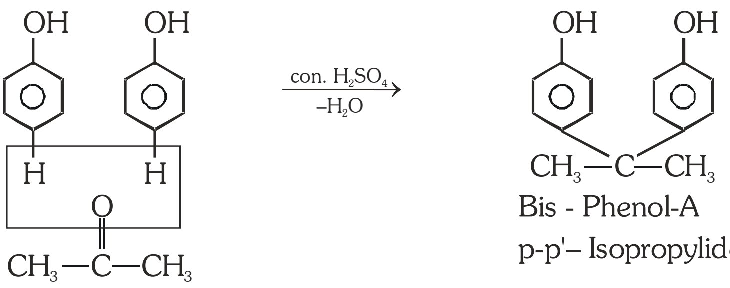
Phthalic anhydride Phenol (2 molecules) Phenolphthalein (Colourless in acidic medium and pink in alkaline medium)

(xi) Lederer Manasse (Condensation with formaldehyde) : Phenol condenses with HCHO (excess) in presence of NaOH or weak acid (H^+) to form a polymer known as bakelite (resin).



Polymer bakelite (Phenol formaldehyde resin)

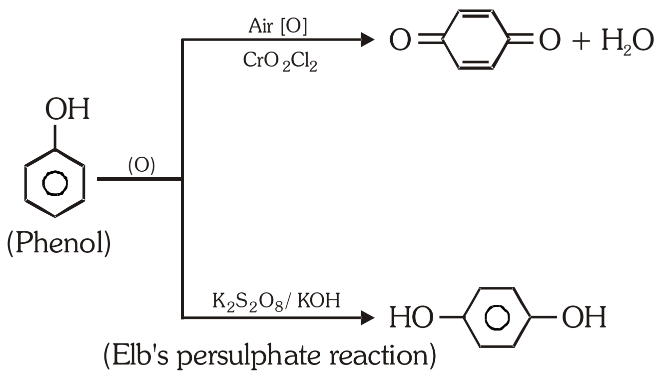
(xii) Reaction with acetone: (Condensation with acetone)



Bis - Phenol-A

p-p'– Isopropylidene diphenol

(xiii) Oxidation:



p-Benzoquionone (Pink)

(Quinol)

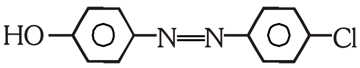
1, 4 – Dihydroxy benzene

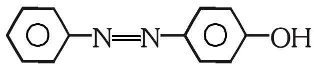
BEGINNER'S BOX-3

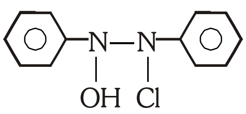
1. Reimer–Tiemann formylation reaction involves addition of :-

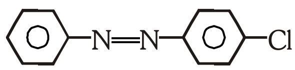
(1) Chloroform on phenoxide ion
(2) Trichloromethyl carbanion on phenoxide ion
(3) Dichlorocarbene on phenoxide ion
(4) Hydroxide ion on phenol

2. Phenol reacts with benzenediazonium chloride solution to form a compound of the structure :-

(1) 

(2) 

(3) 

(4) 

3. Phenol $\xrightarrow[\text{conc.} H_2SO_4]{NaNO_2}$ Green colour $\xrightarrow{H_2O}$ red colour $\xrightarrow{NaOH}$ Blue colour

This reaction is associated with the name of :-

(1) Gattermann
(2) Hofmann
(3) Liebermann
(4) Reimer–Tiemann

Test of Phenol :

(1) Phenol turns blue litmus to red.
(2) Aqueous solution of phenol gives a violet colour with a drop of ferric chloride.
(3) Phenol gives Liebermann's nitroso test.
(4) Aqueous solution of phenol gives a white ppt. of 2,4,6-tribromophenol with bromine water.
(5) Phenol combines with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which gives pink colour with alkali.

Differences between phenol and alcohol (C_2H_5OH) :

(1) Phenol is more acidic than aliphatic alcohol due to resonance in phenoxide ion.

(2) Phenol gives violet colour with $FeCl_3$ while aliphatic alcohol does not give.

(3) Phenol gives triphenyl phosphate with PCl_5 while aliphatic alcohol does not.

(4) Phenol on oxidation gives quinone while alcohol gives aldehyde or ketone and acids.

Uses of Phenol :

Phenol is used :

(1) As an antiseptic in soaps and lotions. "Dettol" (mixture of chloroxylenol and terpineol)

(2) In manufacture of azodyes, phenolphthalein, picric acid (explosive), cyclohexanol (Solvent for rubber), plastics (bakelite) etc.

(3) In manufacture of drugs like aspirin, salol, phenacetin etc.

(4) As preservative for ink.

5.0 ETHER

R—O—R (Dialkyl ether), alkoxy alkane. It's General formula is $C_nH_{2n+2}O$.

$CH_3—O—CH_2CH_3$ (Methoxy ethane) or Ethyl methyl ether

Ether is monoalkyl derivative of R–OH and dialkyl derivative of H_2O

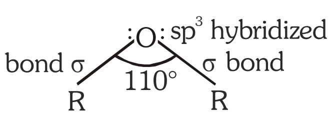
$$R—OH \xrightarrow[+R]{-H} R—O—R \xleftarrow[+2R]{-2H} H—O—H$$

Classification : They may be classified as :

(a) Simple or symmetrical ether. e.g. R–O–R

(b) Mixed or unsymmetrical ether e.g. R–O–R'

Structure :



The molecule of ether is bent due to presence of lone pair. The bond angle is 110^0. It is greater than that of water (105^0) due to the repulsion between bulkier alkyl groups. Due to bent structure, it posses dipole moment and hence are polar molecules.

5.1 General Methods of Preparation

(a) From alkyl halides :

(i) By Williamson's synthesis :

$$R—X + NaO—R \longrightarrow R—O—R + NaX \text{ [S}_N2 \text{ Reaction]}$$

Ex. $CH_3—CH_2—Cl + CH_3—ONa \longrightarrow CH_3—CH_2O—CH_3 + NaCl$

Ex. $\boxed{(CH_3)_3C—Cl + CH_3ONa \longrightarrow H_2C{=}C(CH_3)—CH_3 \text{ (Major)}}$ 3° RX fails to give ethers

Ex. $(CH_3)_3C—ONa + CH_3—CH_2—Cl \xrightarrow{\Delta} (CH_3)_3C—O—CH_2—CH_3$

Ex. $CH_2{=}CH—Cl + CH_3CH_2—ONa \longrightarrow$ No reaction

[Stable by Resonance]

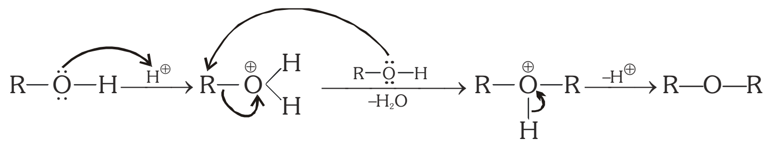
(ii) Reaction with Dry Ag_2O : $2RX + Ag_2O \xrightarrow{\Delta} R{-}O{-}R + 2AgX$

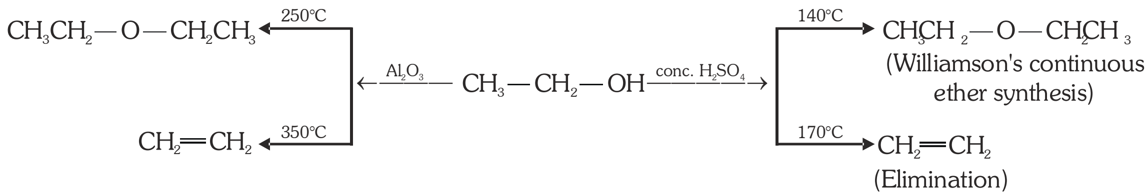
Ex. $2CH_3{-}CH_2{-}Cl + Ag_2O \xrightarrow{\Delta} CH_3CH_2OCH_2CH_3 + 2AgCl$

(b) From R–OH:

(i) By Bimolecular dehydration : $R{-}OH \xrightarrow[\Delta]{\text{Con. } H_2SO_4} R{-}O{-}R$

Mechanism :





(ii) Reaction with CH_2N_2 (diazomethane) :

$$R{-}OH + CH_2N_2 \xrightarrow[BF_3]{\Delta} R{-}O{-}CH_2{-}H + N_2$$

5.2 Physical Properties

(i) CH_3OCH_3 , $CH_3OCH_2CH_3$ are gases and higher ethers are volatile liquids.

(ii) Ether are less polar.

(iii) Ethers are less soluble in H_2O.

(iv) Ethers have less BP then corresponding alcohol.

Illustrations

Illustration 5. Ethers are less soluble in H_2O . Why ?

Solution. Due to less polarity, it forms weaker H–Bonding with H_2O.

Illustration 6. Ethers have less BP than corresponding alcohol. Why ?

Solution. No H–Bonding in ether molecules.

5.3 Chemical properties

Ethers are less polar so less reactive and do not react with active metals [Na,K], cold dil. acid, oxidising and reducing agent. They do not have any active functional group.

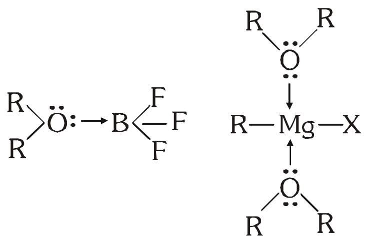
(1) Basic nature : Due to presence of ℓ.p on oxygen atom ether behave as lewis base

Ethers react with cold conc. acid and form oxonium salts.

Ex. $C_2H_5\ddot{O}C_2H_5 \xrightarrow{\text{cold ; conc. HCl}} \left[C_2H_5{-}\overset{\oplus}{\underset{|\,H}{O}}{-}C_2H_5\right]Cl^{\ominus}$ (diethyl oxonium chloride)

Ex. $C_2H_5-\ddot{\underset{\cdot\cdot}{O}}-C_2H_5 \xrightarrow[H_2SO_4]{\text{cold ; conc.}} \left[C_2H_5-\overset{\oplus}{\underset{|\atop H}{O}}-C_2H_5\right]HSO_4^{\ominus}$ (diethyl oxonium hydrogen sulphate)

Ethers form dative bond with Lewis acids like BF_3, $AlCl_3$, RMgX etc.

Ex.  [Ether is used as a solvent] for Grignard reagent.

(2) Formation of peroxides : Ether add up atmospheric oxygen or ozonised oxygen. It is explained by Free radical mechanism as intermediate is free radical.

$$C_2H_5-O-C_2H_5 \xrightarrow[\text{Long contact}]{O_2\,(\text{nonpolar})} CH_3CH_2-O-\underset{|\atop O-O-H}{CHCH_3}$$

sunlight or UV

$$C_2H_5\ddot{O}C_2H_5 + \ddot{O} \longrightarrow C_2H_5\underset{\downarrow\atop :\ddot{O}:}{\ddot{O}}C_2H_5 \text{ or } (C_2H_5)_2O \longrightarrow O$$

$$CH_3CH_2-O-CH_2-Ph \xrightarrow[\text{long contact}]{O_2} CH_3-CH_2-O-\overset{H}{\dot{C}H}-Ph \xrightarrow{O_2} CH_3-CH_2-O-\underset{|\atop O-O-H}{CH}-Ph$$

Peroxides are unstable and explosives.

GOLDEN KEY POINTS

- Test for peroxides
  Ether (peroxide) $\xrightarrow{FeSO_4/KCNS}$ Red colour
  Ether (Peroxides) + $Fe^{+2} \longrightarrow Fe^{+3} \xrightarrow{CNS^{\ominus}} \underset{(\text{Red})}{Fe(CNS)_3}$

(3) Reaction with PCl_5 : $ROR + PCl_5 \xrightarrow{\text{heat}} 2RCl + POCl_3$

(4) Reduction : $CH_3CH_2OCH_2CH_3 \xrightarrow[\text{heat}]{\text{Red P + HI}} 2CH_3CH_3$

(5) Reaction with HX : R–O–R' + HI $\longrightarrow$ R–OH + R'–I

Uses of ether :

(i) General anaesthetic agent.

(ii) Solvent for oil, fats, resins, Grignard reagent.

(iii) For providing inert & moist free medium to organic reaction e.g. Wurtz reactions.

(iv) In perfumery.

(v) Di-isopropyl ether $\longrightarrow$ In petrol as an antiknock comp.

(vi) Mixture of alcohol and ether is used as a substitute of petrol. Trade name **"Natalite"**

6.0 CARBONYL COMPOUNDS

Organic Compounds having $>C{=}O$ group are called carbonyl compounds and $>C{=}O$ group is known as carbonyl group. It's general formula is $C_n H_{2n}O$ (n = 1, 2, 3......) Carbonyl compounds are grouped into two categories.

(a) Aldehydes : Aldehyde group is $-\overset{\overset{\displaystyle O}{\|}}{C}-H$ (also known as formyl group). It is a monovalent group

Carbon atom of $-\overset{\overset{\displaystyle O}{\|}}{C}-H$ group is of 1° nature i.e. $\boxed{R-\overset{1^\circ}{\underset{\underset{\displaystyle H}{|}}{C}}{=}O}$

(b) Ketones : The carbonyl group ($>C{=}O$) is a Ketonic group when its both the valencies are satisfied by alkyl group. It is a bivalent group.

Carbon atom of $>C{=}O$ group is of 2° nature i.e. $\boxed{\begin{matrix}R\\R\end{matrix}>\overset{2^\circ}{C}{=}O}$

Ketones are further classified as :

(i) **Simple or Symmetrical ketones** : Having two similar alkyl groups. $\begin{matrix}R\\R\end{matrix}>C{=}O$

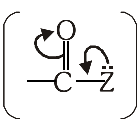
(ii) **Mixed or unsymmetrical ketones** : Having two different alkyl groups. $\begin{matrix}R\\R'\end{matrix}>C{=}O$

Ex. (Ketones) :

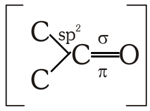
Symmetrical	Unsymmetrical
$\begin{matrix}CH_3\\CH_3\end{matrix}>C{=}O$	$\begin{matrix}CH_3CH_2\\CH_3\end{matrix}>C{=}O$
(Acetone or Dimethyl ketone) Propanone	(Ethyl methyl ketone) Butanone

Sp. Point : $-\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{O}H,\ -\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{X},\ -\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{N}H_2,\ -\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{O}R,$

In all the compounds given above, lone pair of electrons and double bond are in conjugate system.


so resonance occurs. These compounds have $-\overset{\overset{\displaystyle O}{\|}}{C}-$ group still they are not carbonyl compounds because these compounds have characteristic reactions different from carbonyl compounds.

Structure : In $>C{=}O$ compounds C-atom is sp^2 hybridised which forms two σ bonds and one π bond. The unhybridised atomic orbital of C-atom and the parallel 2p orbital of oxygen forms the π bond in $>C{=}O$ group



The C—C—O / H—C—O bond angle is of 120^0

Due to electro-negativity difference in C & O atoms, the $>C=O$ group is polar.

$>\overset{\delta+}{C}=\overset{\delta-}{O}$ Hence aldehydes and Ketones posses considerable dipole moment.

6.1 General Methods of Preparation

(A) For both Aldehydes and Ketones

(1) By Oxidation of Alcohols :

(a) By $K_2Cr_2O_7$ / H_2SO_4 : Oxidation of primary alcohols gives aldehyde and oxidation of secondary alcohols gives Ketones.

$$RCH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4(dil.)]{[O]} RCHO \quad \text{(Aldehyde)}$$

$$R-\underset{\underset{OH}{|}}{CH}-R \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} R-\underset{\underset{O}{\|}}{C}-R \quad \text{(Ketone)}$$

Aldehydes are quite susceptible to further oxidation to acids -

$$RCH_2OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} R-COOH$$

Thus oxidation of primary alcohols is made at the temperature much above the boiling point of aldehyde and thus aldehydes are vapourised out and prevented from being oxidised.

(b) Mild Oxidising Agent : 1° alcohols will get oxidised with CrO_3 / Pyridine, **(collin's reagent) or** P.C.C (Pyridinium chloro chromate $CrO_3 + C_5H_5N + HCl$) to aldehyde and 2° alcohols to ketone.

$$RCH_2OH + [O] \longrightarrow RCHO + H_2O$$

By this reaction, **good yield of aldehyde** is possible.

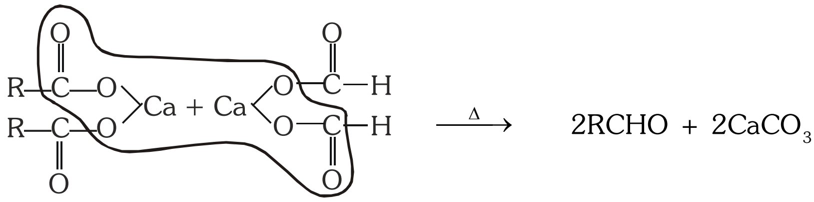
(2) Dehydrogenation of alcohols :

$$CH_3CH_2OH \xrightarrow[300^{\circ}C]{Cu} CH_3CHO \quad \text{(Acetaldehyde)}$$

$$CH_3-\underset{\underset{OH}{|}}{CH}CH_3 \xrightarrow[300^{\circ}C]{Cu} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \quad \text{(Acetone)}$$

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[300^{\circ}C]{Cu} CH_3-\overset{\overset{CH_2}{\|}}{\underset{\underset{CH_3}{|}}{C}} + H_2O \quad \text{(Isobutylene)}$$

(3) By dry distillation of Ca-salts of carboxylic acid :



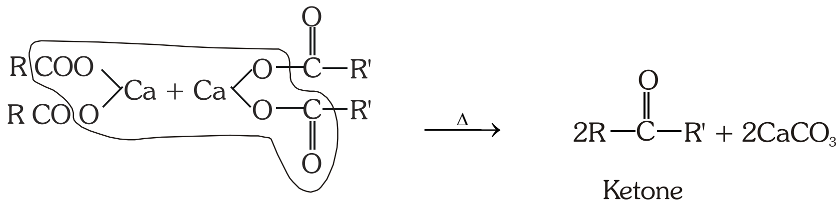
Calcium alkanoate Calcium formate ($R-\overset{O}{\overset{\|}{C}}-R$ and HCHO are also formed)

$$\begin{matrix} H\,COO \\ HCO\,O \end{matrix} > Ca \xrightarrow{\Delta} HCHO + CaCO_3$$

$$\begin{matrix} R\,COO \\ RCO\,O \end{matrix} > Ca \xrightarrow{\Delta} \begin{matrix} R \\ R \end{matrix} > C{=}O + CaCO_3$$

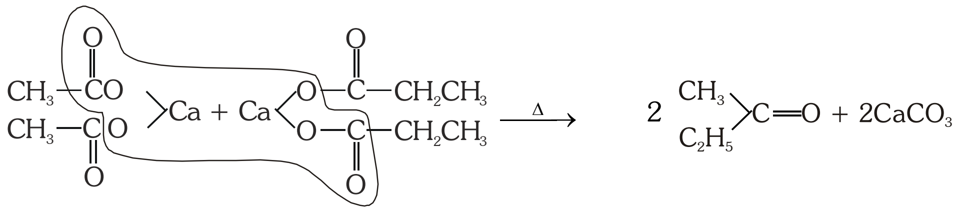
Calcium-alkanoate Ketone

Calcium salts of acids other than formic acid on heating together give unsymmetrical ketone



Ketone

To prepare ethyl methyl ketone Calcium acetate and Calcium propionate are used :



Calcium Acetate Calcium propionate Ethyl methyl ketone

(4) By Thermal decomposition of carboxylic acids : Vapour of carboxylic acids when passed over MnO/300^{0}C give carbonyl compounds

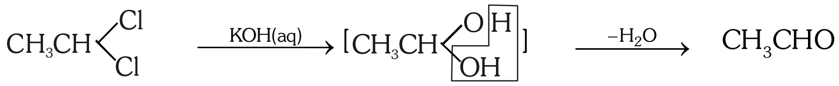
$$\begin{matrix} H\,COOH \\ HCO\,OH \end{matrix} \xrightarrow[300°C]{MnO} HCHO + H_2O + CO_2$$

$$\begin{matrix} CH_3CO\,OH \\ CH_3\,COOH \end{matrix} \xrightarrow[300°C]{MnO} \begin{matrix} CH_3 \\ CH_3 \end{matrix} > C{=}O + CO_2 + H_2O$$

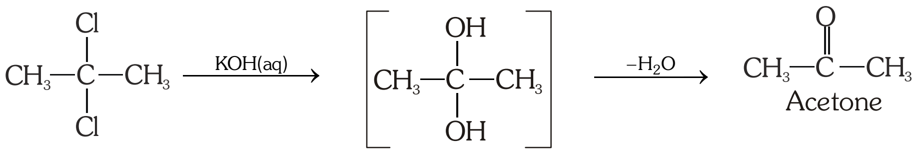
$$\begin{matrix} RCO\,OH \\ H\,COOH \end{matrix} \xrightarrow[300°C]{MnO} RCHO + CO_2 + H_2O$$

$$\begin{matrix} RCO\,OH \\ R'\,COOH \end{matrix} \xrightarrow[300°C]{MnO} RCOR' + CO_2 + H_2O$$

(5) By Hydrolysis of gem dihalides : Terminal gem-dihalides on hydrolysis give aldehydes while the non-terminal gem-dihalides give ketones.



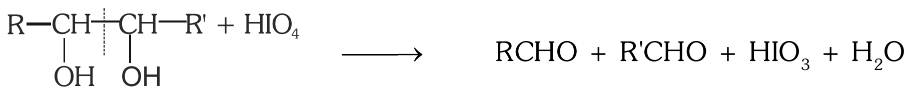
Terminal gem-dihalide [unstable] Acetaldehyde

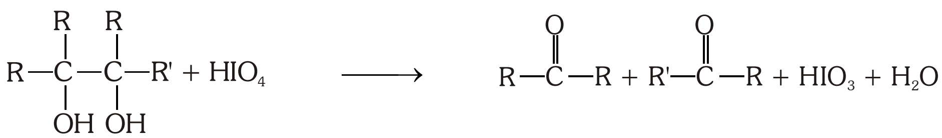


Non terminal gem-dihalide

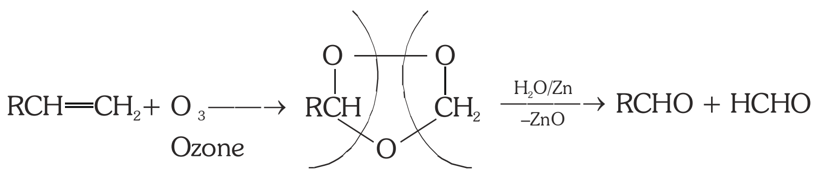
unstable

(6) By Oxidation of diols : With periodic acid (HIO_4) or lead tetra acetate $(CH_3COO)_4$ Pb vicinal diols get oxidised to form carbonyl compounds

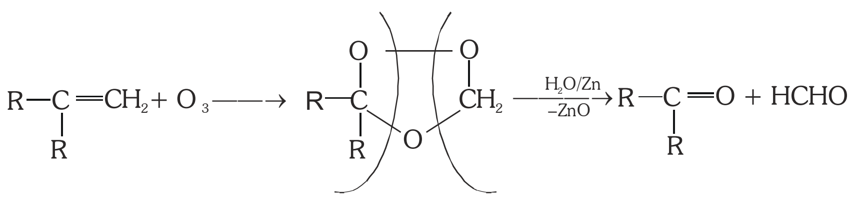




(7) By Ozonolysis of alkenes : This reaction is used to determine the position of double bond in alkene. Zn is used to decompose H_2O_2 formed during hydrolysis.

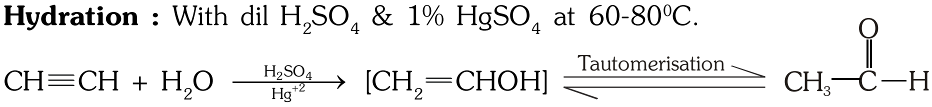


Ozone Ozonide

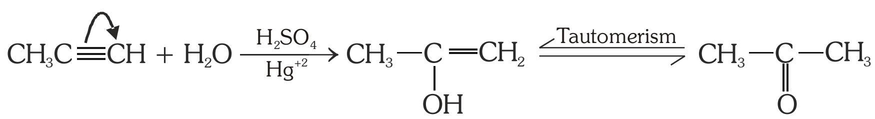


(8) From Alkyne :

(a) Hydration : With dil H_2SO_4 & 1% $HgSO_4$ at 60-80°C.



Other alkynes mainly give ketone :



(enol)

(b) Hydroboration : Reaction with B_2H_6 or R_2BH give alkenyl dialkyl borane.

$$\boxed{\begin{array}{l} \textbf{1 – alkyne gives} \longrightarrow \textbf{aldehyde} \\ \textbf{other alkynes} \longrightarrow \textbf{ketone} \end{array}}$$

$$R{-}C{\equiv}CH + \overset{+\delta-\delta}{R_2BH} \longrightarrow R{-}CH{=}CHBR_2 \xrightarrow[OH^-]{H_2O_2} RCH{=}CHOH \xrightleftharpoons{\text{Tautomerism}} R{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}H + R_2BOH$$

$$CH_3{-}C{\equiv}C{-}CH_3 + R_2BH \longrightarrow CH_3{-}CH{=}\underset{\underset{BR_2}{|}}{C}{-}CH_3 \xrightarrow[OH^-]{H_2O_2}$$

$$CH_3{-}CH{=}\underset{\underset{OH}{|}}{C}{-}CH_3 \rightleftharpoons CH_3{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3$$

(B) For Aldehydes only

(1) Rosenmund's reduction :

$$RCOCl + H_2 \xrightarrow{Pd} RCHO \longrightarrow RCH_2OH$$

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

$BaSO_4$ controls the further reduction of aldehyde to alcohols. Formaldehyde can not be prepared by this method.

Ex. $C_2H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_2H_5CHO + HCl$

Propionyl Chloride Propanal

(2) Stephen's reduction :

$$R{-}C{\equiv}N{+}2H \xrightarrow{SnCl_2/HCl} R{-}CH{=}NH \xrightarrow{H_2O} RCHO{+}NH_3$$

$$C_2H_5{-}C{\equiv}N + 2[H] \xrightarrow{SnCl_2/HCl} C_2H_5CH{=}NH \xrightarrow{H_2O} C_2H_5CHO + NH_3$$

(C) For Ketones only

(1) From Grignard's reagent :

$$RMgX + R{-}C{\equiv}N \longrightarrow R{-}\underset{\underset{R}{|}}{C}{=}NMgX \xrightarrow{2H_2O} R{-}\underset{\underset{R}{|}}{C}{=}O + NH_3 + Mg\begin{smallmatrix} X \\ OH \end{smallmatrix}$$

$$\underset{\text{(Limited)}}{RMgX} + R{-}\overset{\overset{O}{\|}}{C}{-}Cl \longrightarrow R{-}\overset{\overset{O}{\|}}{C}{-}R$$

$$\underset{\text{(Limited)}}{RMgX} + R{-}\overset{\overset{O}{\|}}{C}{-}OR \xrightarrow{\Delta} R{-}\overset{\overset{O}{\|}}{C}{-}R + ROMgX$$

(2) From dialkyl Cadmium : R'CdR' (dialkyl Cadmium) is an organometallic compound.

$$RCOCl + R'CdR' \longrightarrow RCOR' + R'CdCl$$

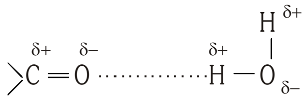
This reaction is superior than Grignard Reaction because the ketones formed, further reacts with Grignard reagent to form 3° alcohols.

Ex. $CH_3COCl + \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!Cd \longrightarrow \begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!C{=}O + \begin{matrix} C_2H_5 \\ Cl \end{matrix}\!\!>\!Cd$

6.2 Physical Properties

State : Only formaldehyde is gas, all other carbonyl compounds upto C_{11} are liquids and C_{12} & onwards solid.

Solubility : C_1 to C_3 (formaldehyde, acetaldehyde and propionaldehyde) and acetone are freely soluble in water due to polarity of $>\overset{\delta+}{C}=\overset{\delta-}{O}$ bond and can form H—bond with water molecule. C_5 onwards are insoluble in water.



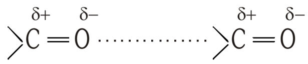
$$\boxed{\text{Solubility} \propto \frac{1}{\text{Molecular weight}}}$$

H-bonding

Boiling point : $\boxed{\text{Boiling point} \propto \text{Molecular weight}}$

Boiling point order is - $\boxed{\textbf{Alcohol > Ketone > Aldehydes > Alkane}}$ (of comparable molecular mass)

This is because in alcohols intermolecular H-bonding is present but in carbonyl compounds H-bonding doesn't exist, instead dipole-dipole & vander waal force of attraction is present. Alkanes are non polar.



Density : Density of carbonyl compounds is lower than water.

BEGINNER'S BOX-4

1. Acids do not give the characteristic reactions of C=O group because of :-

(1) Dimerisation (2) Resonance (3) Cyclic structures (4) Attached alkyl redical

2. The vapour density of a compound is 45. Its molecular formula will be -

(1) C_2H_5O (2) $C_3H_6O_2$ (3) $C_4H_{10}O$ (4) $C_5H_{14}O$

3. 23 gm of sodium of reaction with methyl alcohol gives :

(1) Half mole of H_2 (2) One mole of H_2 (3) One mole of O_2 (4) none

6.3 Chemical Properties

Carbonyl compounds undergo following reactions :

6.3.1 Nucleophilic addition reactions (Already discussed in Reaction Mechanism Part-2)

6.3.2 Other reactions

6.3.3 Reactions of only aldehyde

6.3.4 Reactions of only ketones

6.3.2 Other reactions

(a) Reduction : The nature of product depends upon the reducing agent used.

(i) $\boxed{>C{=}O \longrightarrow >CH_2}$ Reducing agents are

- Red P/HI at 150°C
- Zn-Hg/HCl [Clemensen's reduction]
- (i) N_2H_4 (ii) $\overset{\ominus}{O}H/\Delta$ [Wolf Kishner reduction]

(ii) $\boxed{>C{=}O \longrightarrow >CHOH}$ Reducing agents are

- Metal + H_2
- $LiAlH_4$
- $NaBH_4$
- Na + C_2H_5OH

(b) Reaction with PCl_5 & $SOCl_2$:

$$>C{=}O + PCl_5 \longrightarrow >C<^{Cl}_{Cl} + POCl_3$$

Phosphorus penta chloride

$$>C{=}O + SOCl_2 \longrightarrow >C<^{Cl}_{Cl} + SO_2$$

Thionyl chloride

(c) Aldol Condensation : Carbonyl compounds which contain α-H atoms undergo condensation with dil. NaOH to give aldol. Aldol contains both alcoholic and carbonyl group, which on heating in alkaline medium gets converted into α, β-unsaturated carbonyl compound.

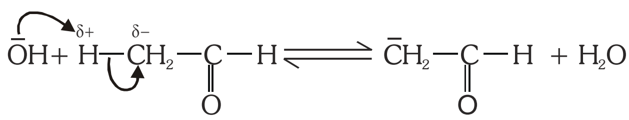
$$CH_3-\underset{\underset{O}{\|}}{C}H + HCH_2CHO \xrightarrow[NaOH]{dil} CH_3-\underset{\boxed{OH}}{CH}-\underset{\boxed{H}}{CH}-CHO \xrightarrow[-H_2O]{\overset{\ominus}{O}H/\Delta} \underset{\text{Crotonaldehyde}}{CH_3-CH{=}CH-CHO}$$

Mechanism of aldol condensation : It takes place in the following two stages :

(i) Formation of Carbanion

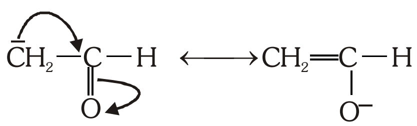
(ii) Combination of carbanion with other carbonyl molecule.

(i) Formation of Carbanion : α-H atom of $>C{=}O$ group are quite acidic which can be removed easily as proton, by a base

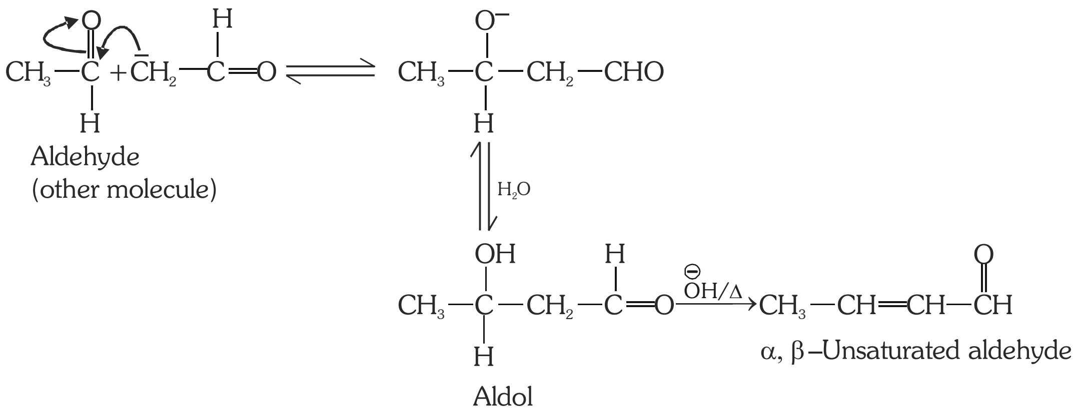


Base Acetaldehyde Carbanion

Carbanion thus formed is stable because of resonance -

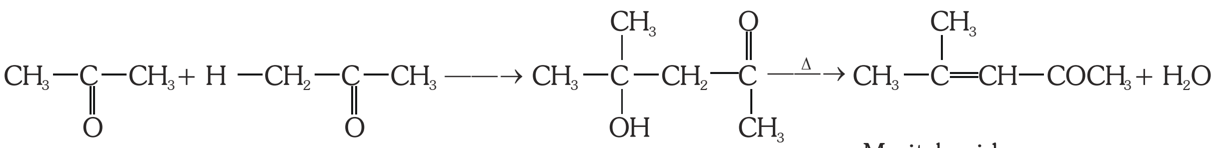


(ii) Combination of carbanion with other carbonyl molecule :



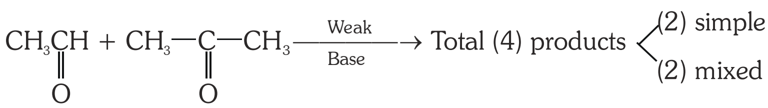
Identical carbonyl compounds ⟶	Simple or self aldol condensation.
Different carbonyl compounds ⟶	Mixed or crossed aldol condensation.

Simple or Self condensation :

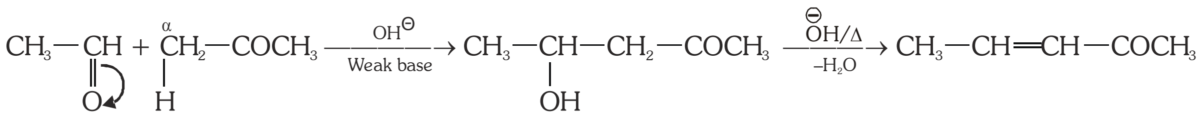


Mesityl oxide or
4–Methylpent– 3–en– 2–one

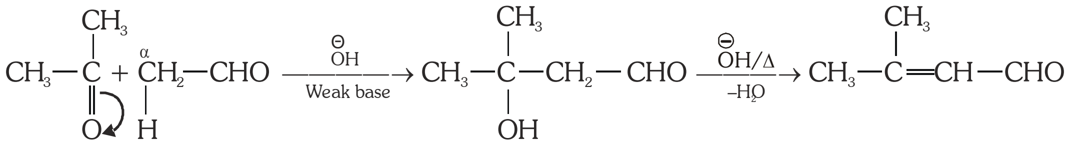
Mixed or Crossed aldol Condensation :



Mixed aldol condensation products of the above reaction are :



(Aldol)



(Aldol)

Illustrations

Illustration 7. $CH_3CHO + CH_3CH_2CHO \xrightarrow[(WB)]{\ominus OH}$ Total 4 products. Write structure of products ?

Solution.

$$CH_3-\underset{\underset{O}{\|}}{C}H + \underset{\underset{H}{|}}{C}H_2CHO \xrightarrow{\ominus OH} (Aldol) \xrightarrow[-H_2O]{\overset{\ominus}{O}H/\Delta} CH_3-CH=CH-CHO$$

$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}H + \underset{\underset{H}{|}}{\overset{\alpha}{C}}H_2-CHO \xrightarrow{\ominus OH} (Aldol) \xrightarrow[-H_2O]{\overset{\ominus}{O}H/\Delta} CH_3-CH_2-CH=CH-CHO$$

$$CH_3-\underset{\underset{O}{\|}}{C}H + \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|\alpha}}{C}}H-CHO \xrightarrow{\ominus OH} (Aldol) \xrightarrow[-H_2O]{\overset{\ominus}{O}H/\Delta} CH_3-CH=\overset{\overset{CH_3}{|}}{C}-CHO$$

$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}H + \underset{\underset{H}{|}}{\overset{\overset{CH_3}{\alpha|}}{C}}H-CHO \xrightarrow{\ominus OH} (Aldol) \xrightarrow[-H_2O]{\overset{\ominus}{O}H/\Delta} CH_3-CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CHO$$

GOLDEN KEY POINTS

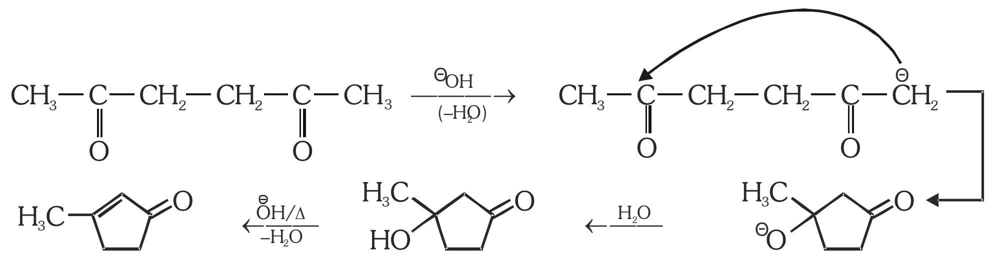
- If in crossed aldol condensation reaction , only one carbonyl compound have α–H then total two products are formed.

$$CH_3CHO + C_6H_5CHO \xrightarrow[(WB)]{\ominus OH} \text{Total 2 product.}$$

$$CH_3-\underset{\underset{O}{\|}}{C}H + \underset{\underset{H}{|}}{\overset{\alpha}{C}}H_2-CHO \xrightarrow{\ominus OH} (Aldol) \xrightarrow[-H_2O]{\overset{\ominus}{O}H/\Delta} \underset{\text{(Crotonaldehyde)}}{CH_3-CH=CH-CHO}$$

$$C_6H_5-\underset{\underset{O}{\|}}{C}H + \underset{\underset{H}{|}}{\overset{\alpha}{C}}H_2-CHO \xrightarrow{\ominus OH} (Aldol) \xrightarrow[-H_2O]{\overset{\ominus}{O}H/\Delta} \underset{\text{(Cinnamaldehyde)}}{C_6H_5-CH=CH-CHO}$$

- **Intramolecular** aldol condensation :



(α,β – Unsaturated Ketone) (Aldol)

Here one more product having 3 membered ring is also possible, but 5 membered ring is more stable than 3 membered ring so above product is formed as a major product.

(d) Oxidation reactions :

(i) By $K_2Cr_2O_7/H_2SO_4$: On oxidation with $K_2Cr_2O_7/H_2SO_4$ 1° alc. gives aldehyde, which on further oxidation gives acid with same number of carbons. If 2° alcohol is oxidised at elevated temperature using $KMnO_4/H^{\oplus}$, it gets oxidised to give acids with less number of C-atom.

$$\underset{(1^\circ \text{ alcohol, 2C})}{H_3C{-}CH_2OH} \xrightarrow{[O]} H_3C{-}CH{=}O \xrightarrow{[O]} \underset{\text{(Acid with 2C-atoms)}}{H_3C{-}COOH}$$

$$\underset{(2^\circ \text{ alcohol with 5C})}{CH_3CH_2CH_2{-}\underset{\substack{|\\OH}}{CH}{-}CH_3} \xrightarrow{[O]} CH_3CH_2CH_2{-}\underset{\substack{\|\\O}}{C}{-}CH_3 \xrightarrow{[O]} \underset{\text{(Acids having less number of C)}}{CH_3CH_2COOH + CH_3COOH}$$

(ii) SeO_2 (Selenium dioxide) : Ketones or aldehydes on oxidation with SeO_2 give dicarbonyl compounds. This reaction is possible only in compounds containing α–CH_2– unit.

HCHO doesn't show this reaction.

$$\overset{\alpha}{C}H_3CHO + SeO_2 \xrightarrow{\Delta} H{-}\underset{\substack{\|\\O}}{C}{-}\underset{\substack{\|\\O}}{C}{-}H + Se + H_2O$$

Glyoxal

$$CH_3{-}\underset{\substack{\|\\O}}{C}{-}\overset{\alpha}{C}H_3 + SeO_2 \xrightarrow{\Delta} CH_3{-}\underset{\substack{\|\\O}}{C}{-}\underset{\substack{\|\\O}}{C}{-}H + Se + H_2O$$

Methyl glyoxal (Pyruvaldehyde)

6.3.3 Reactions of only aldehydes :

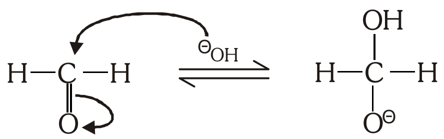
(a) Cannizaro's reaction : Those aldehydes which do not contain α - H atom give this reaction, with conc. NaOH or KOH; Products are Salt of carboxylic acid + alcohol

In this reaction one molecule of carbonyl compounds is oxidised to acid, while other is reduced to alcohol, such type of reactions are called redox reaction.

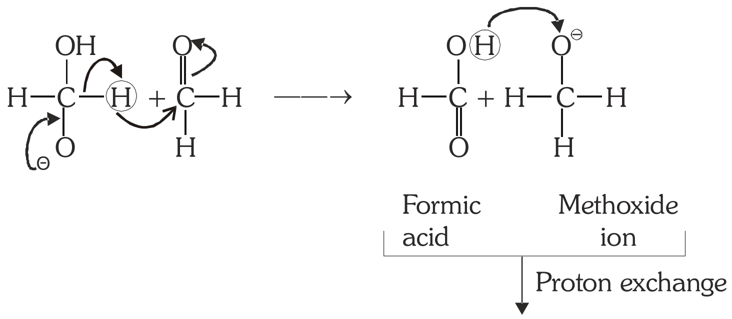
$$HCHO + HCHO \xrightarrow[\text{NaOH},\Delta]{\text{Conc.}} HCOONa + CH_3OH$$

Mechanism involved in cannizaro's reaction :

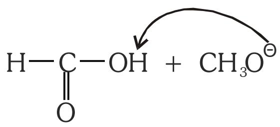
(a) Rapid reversible addition of $\bar{O}H$ to one molecule of HCHO.



(b) Transfer of hydride ion $\overset{\ominus}{H}$ to second molecule of HCHO



(c) Proton exchange



$$\longrightarrow HCOO^{\ominus} + CH_3OH$$

$$HCOO^{\ominus} + Na^{\oplus} \longrightarrow HCOONa$$

When molecules are same	$\longrightarrow$ Simple cannizaro reaction (disproportionation reaction)
Two different molecules	$\longrightarrow$ Mixed cannizaro reaction (Redox reaction)

In mixed or crossed cannizaro reaction more reactive aldehyde is oxidised and less reactive aldelyde is reduced.

$$HCHO + C_6H_5CHO \xrightarrow[\Delta]{NaOH} \underset{\substack{\text{Oxidized} \\ \text{(Sodium formate)}}}{HCOONa} + \underset{\substack{\text{Reduced} \\ \text{(Benzyl alcohol)}}}{C_6H_5CH_2OH}$$

(b) Tischenko reaction : It is a modified cannizaro reaction. All aldehydes undergo this reaction in presence of $(C_2H_5O)_3Al$, to form ester.

$$2RCHO \xrightarrow[\Delta]{(C_2H_5O)_3Al} \underset{\text{Ester}}{RCH_2-O-\overset{\overset{\large O}{\|}}{C}-R}$$

Ex. $CH_3CHO + CH_3CHO \xrightarrow{(C_2H_5O)_3Al} \underbrace{CH_3COOH + CH_3CH_2OH}_{\text{Esterification}\downarrow}$

$$CH_3-COOCH_2CH_3 \text{ (Ethyl acetate)}$$

(c) Reducing character : Aldehydes are easily oxidised so they are strong reducing agents.

(i) Tollen's reagent : It oxidises aldehydes. Tollen's reagent is ammonical silver nitrate solution

$$(AgNO_3+NH_4OH) \longrightarrow [Ag(NH_3)_2]OH$$

$$RCHO+[Ag(NH_3)_2]OH \longrightarrow RCO\overset{\ominus}{O} + \underset{\text{Silver mirror}}{Ag} + H_2O$$

$$AgNO_3 + NH_4OH \longrightarrow AgOH \longrightarrow Ag_2O$$

$$RCHO + Ag_2O \longrightarrow RCO\overset{\ominus}{O} + Ag\downarrow \text{ (Silver mirror)}$$

(ii) Fehling's solution : It is a mixture of aqueous $CuSO_4$, NaOH and sodium potassium tartarate.

Fehling solution A– (aq.) solution of $CuSO_4$

Fehling solution B– Roschelle salt (Sodium potassium tartarate + NaOH)

Fehling solution A + Fehlings solution B(Dark blue colour of cupric tartarate)

$$RCHO + Cu^{+2} + OH^{-} \longrightarrow RCO\overset{\ominus}{O} + Cu_2O$$

(Cuprous oxide–Red ppt.)

$$Cu^{2+} \longrightarrow Cu^{+}$$

(Cupric - Blue) (Cuprous - Red ppt.)

(iii) Benedict's solution : It is a mixture of $CuSO_4$ + sodium citrate + NaOH. It provides Cu^{+2}. It is reduced by aldehyde to give red ppt of cuprous oxide.

$$RCHO + Cu^{2+} + OH^{-} \longrightarrow RCO\overset{\ominus}{O} + Cu_2O$$

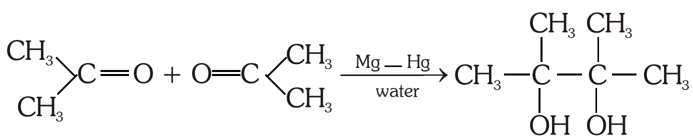
(Cuprous oxide–Red ppt.)

(iv) Schiff's reagent : Dilute solution of p-rosaniline hydrochloride or magenta dye, is a pink coloured dye and is known as schiff' dye.

Its pink colour is discharged by passing SO_2 gas and the colourless solution obtained is called schiff's reagent, Aldehyde reacts with this reagent to restore the pink colour.

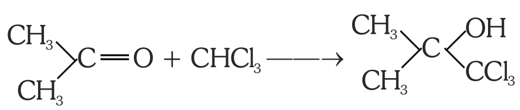
6.3.4 Reaction of Only Ketones

(1) Reduction : Acetone is reduced by magnesium amalgam and water to give pinacol.



Pinacol

(2) Reaction with chloroform :



(Chloretone)
(Hypnotic compound)

(3) Oxidation reaction : According to popoff's rule $>C=O$ group stays with smaller alkyl group.

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{[O]} CH_3COOH + CH_3COOH$$

BEGINNER'S BOX-5

1. The compounds capable in reaction with Tollen's reagent is (are) :

(1) Formaldehyde (2) Formic acid (3) Acetaldehyde (4) All the above

2. Acetaldehyde reacts with NaOH to form :-

(1) $CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-\overset{H}{\overset{|}{C}}=O$

(2) $CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{H}{\overset{|}{C}}=O$

(3) $CH_3-\underset{OH}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-CH_3$

(4) $\underset{OH}{\underset{|}{CH_2}}-CH_2-CH_2-\underset{H}{\underset{|}{C}}=O$

3. Fehling's solution is a :-

(1) Solution of magenta dye bleached by SO_2

(2) Ammonical solution of $AgNO_3$

(3) Mixture of a solution of $CuSO_4$ and a solution of caustic soda and sodium potassium tartarate

(4) Alcoholic solution of 2,4-dinitrophenylhydrazine

7.0 BENZALDEHYDE (C_6H_5CHO) [OIL OF BITTER ALMONDS (COMPONENT OF BITTER ALMOND)]

7.1 General Methods of Preparation

$C_6H_6 \xrightarrow{CO/\,HCl\,+\,ZnCl_2}$ (Gattermann-koch aldehyde synthesis)

$C_6H_5CH_3 \xrightarrow{(1)\ CrO_2Cl_2\ \ (2)\ H_2O}$ (Etard reaction)

$C_6H_5COCl \xrightarrow{Pd/BaSO_4}$ (Rosenmund reaction)

$C_6H_5CN \xrightarrow{(i)\ SnCl_2/HCl\ (ii)\ H_2O}$ (Stephen's reaction)

$(C_6H_5COO)_2Ca \xrightarrow{(HCOO)_2Ca/\,\Delta}$

$\longrightarrow C_6H_5CHO$

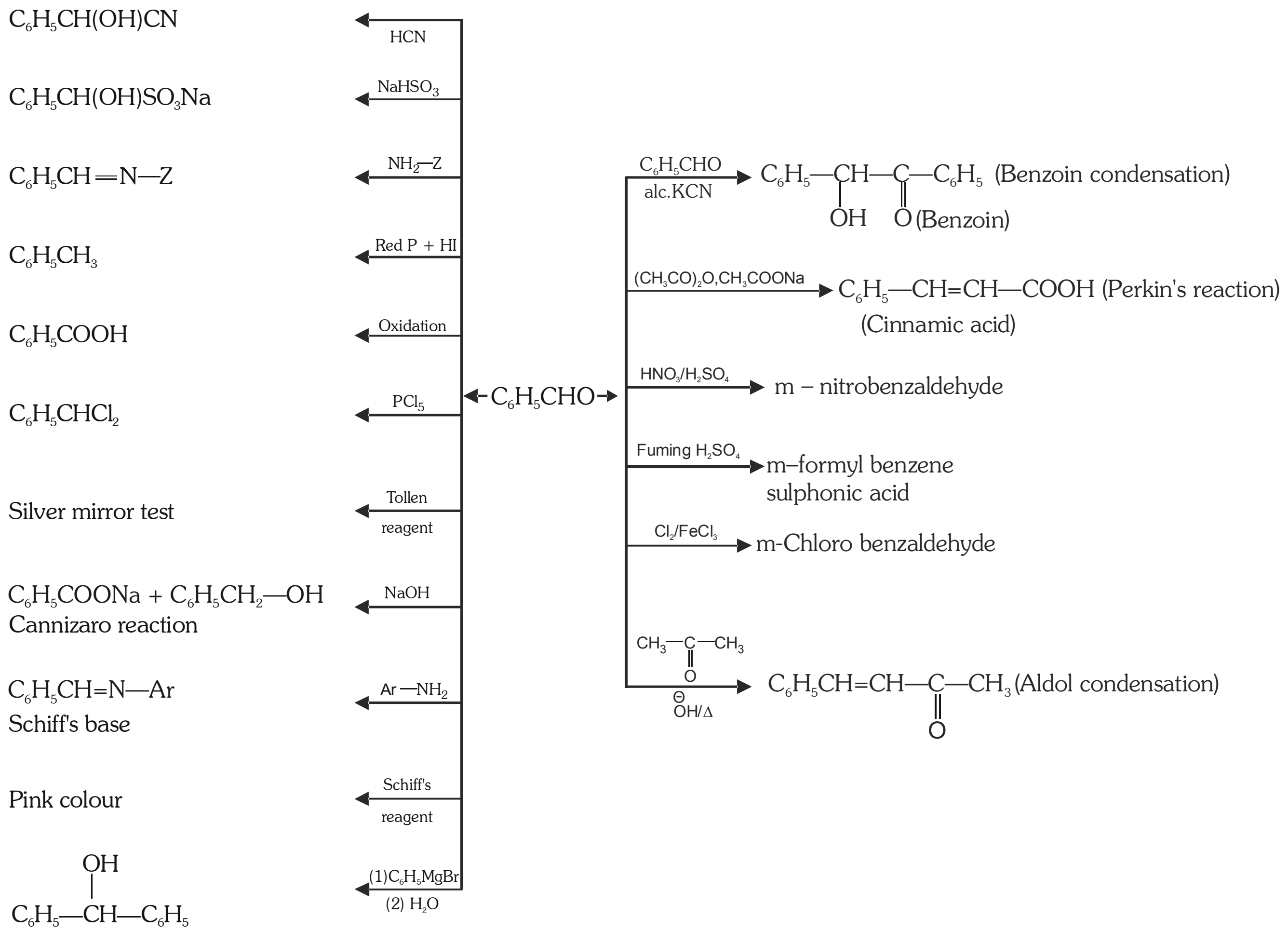
$C_6H_5CHCl_2 \xrightarrow{aq.\ KOH}$

$C_6H_5CH_2OH \xrightarrow{[O]\ (controlled\ oxidation)}$

$C_6H_5MgBr \xrightarrow{HCOOC_2H_5}$

$C_6H_6 \xrightarrow[(2)\ H_2O]{(1)\ HCN/HCl\ +\ ZnCl_2}$ (Gattermann aldehyde synthesis)

7.2 Chemical Properties



8.0 CARBOXYLIC ACID

Organic compounds having –COOH group are called Carboxylic acids. This functional group is composed of Carbonyl ($-\overset{\overset{\large O}{\|}}{C}-$) and hydroxyl (—OH) group.

$$\underset{\text{Carbonyl group}}{-\overset{\overset{O}{\|}}{C}-} \quad + \quad \underset{\text{Hydroxyl group}}{-OH} \quad \longrightarrow \quad \underset{\text{Carboxylic group}}{-\overset{\overset{O}{\|}}{C}-OH}$$

The properties of the carboxylic group are not simply the combined properties of these two groups, but it has its own distinctive properties. The acidic nature of carboxylic acids is due to the presence of replaceable H-atom in the Carboxylic group. The general formula is $C_nH_{2n}O_2$.

Classification :

Monocarboxylic acid (RCOOH) : Having one carboxylic group, also called monobasic acid.

General formula - $C_nH_{2n}O_2$ (n = 1, 2, 3, ...). Higher mono carboxylic acids are called **fatty acids**.

Ex. CH_3COOH acetic acid

Dicarboxylic acid : Having two carboxylic groups, also called dibasic acid.

Ex. $\begin{array}{c} COOH \\ | \\ COOH \end{array}$ Oxalic acid

Tricarboxylic acid : Having three carboxylic groups also called tribasic acid.

Ex. $\begin{array}{c} \quad CH_2COOH \\ | \\ HO-C-COOH \\ | \\ \quad CH_2COOH \end{array}$ Citric acid

Structure : The carbon atom of –COOH group is sp^2 hybridised, this C- atom is in centre and thus bond angle around C-atom is 120^0.

8.1 General Methods of Preparation

8.1.1 By Oxidation of alcohols & carbonyl compounds : Oxidation is carried out by acidified $K_2Cr_2O_7$ or $KMnO_4$.

$$RCH_2OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} RCHO \xrightarrow{[O]} RCOOH$$

Acids are third oxidation products of alkane.

$$R—H \xrightarrow{[O]} R—OH \xrightarrow{[O]} R—CHO \xrightarrow{[O]} R—COOH$$

GOLDEN KEY POINTS

- Aldehyde on oxidation give acids having same no. of C-atoms.
- Ketones on oxidation give acids having less no. of C-atoms.
- Oxidation of Ketones occurs on prolonged treatment with strong oxidising agent.

8.1.2 By hydrolysis of alkane nitriles or cyanides : Complete hydrolysis takes place in acidic medium (dil. HCl). In alkaline medium there is partial hydrolysis.

$$R-C\equiv N \xrightarrow{H_2O/H^{\oplus}} R-\overset{\overset{\large OH}{|}}{C}=NH \xrightleftharpoons{\text{Tautomerism}} R-\overset{\overset{\large O}{\|}}{C}-NH_2 \xrightarrow{H_2O/H^{\oplus}} R-\overset{\overset{\large O}{\|}}{C}-OH + NH_3$$

8.1.3 By alkaline hydrolysis of 1, 1, 1-trihaloalkane :

$$R-C\begin{matrix} Cl \\ -Cl \\ Cl \end{matrix} + 3KOH \xrightarrow[-3KCl]{} R-C\begin{matrix} OH \\ -O\boxed{H} \\ \boxed{OH} \end{matrix} \xrightarrow[-H_2O]{KOH} RCOOK + H_2O \xrightarrow{HCl} RCOOH + KCl$$

8.1.4 By hydrolysis of acid derivatives :

$$R-\overset{\overset{O}{\|}}{C}-Z + H-OH \longrightarrow R-\overset{\overset{O}{\|}}{C}-OH + HZ$$

Z= —Cl, —OCOR, —OR, —NH_2

Reactivity order of acid derivatives : $\boxed{\mathbf{RCOCl > (RCO)_2O > RCOOR > RCONH_2}}$

$$RCOCl \xrightarrow[\text{dil. acid}]{HOH} RCOOH + HCl$$

$$(RCO)_2O \xrightarrow[\text{dil. acid}]{HOH} 2RCOOH$$

$$RCOOR' \xrightarrow[\text{dil. acid}]{HOH} RCOOH + R'OH$$

$$R-CONH_2 \xrightarrow[\text{dil. acid}]{HOH} RCOOH + NH_3$$

8.1.5 From Grignard's reagent :

$$RMgX + O=C=O \longrightarrow R-\overset{\overset{O}{\|}}{C}-OMgX \xrightarrow{H_2O} R-\overset{\overset{O}{\|}}{C}-OH + Mg\begin{matrix}X\\OH\end{matrix}$$

Carbon dioxide

Solid CO_2(dry ice) is used

8.2 Physical Properties

Carboxylic acids from C_1—C_4 are completely soluble in water.

$$\boxed{\text{Solubility} \propto \frac{1}{\text{molecular weight}}}$$

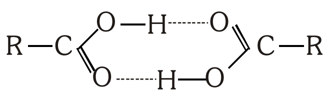
Solubility is due to intermolecular H - bonding with water molecules.

Boiling point : $\boxed{\text{B. P. \& M. P.} \propto \text{Molecular weight,}}$

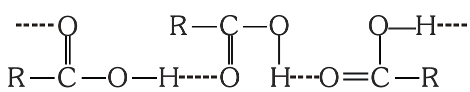
Acids > alcohol

This is because in acids two oxygen atoms take part in H - bonding (while in alcohol only one O - atom takes part).

In vapour or soluble state lower acids occur in the form of dimers.



But in liquid state it exists in polymer form.

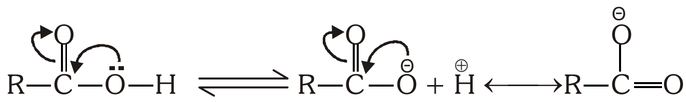


Melting point : Acids having even number of C-atoms have higher melting point as compared to having odd number of C - atoms.The carboxyl group and terminal methyl group in even member acids lie on opposite side to provide more close packing in crystal lattice which results in high melting point.

8.3 Chemical Properties

8.3.1 Reaction due to – H atom of – COOH group

(a) Acidic character :



(Carboxylate ion, Conjugate base)

Carboxylate ion is stabilised by resonance so carboxylic acids show considerable acidic character.

In case of alcohol alkoxide ion is not stabilised so they are neutral.

$$R{-}OH \rightleftharpoons R{-}O^{-} + H^{+}$$

alkoxide ion

(a) Carboxylic acids turn blue litmus to red.

(b) Addition of carboxylic acid to $NaHCO_3$ in water gives out effervescence of CO_2.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$$

(c) Form salts with alkalies.

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

$$RCOOH + Ca(OH)_2 \longrightarrow (RCOO)_2Ca + H_2O$$

(d) Action of metals.

$$RCOOH + Na \longrightarrow RCOONa + \tfrac{1}{2}H_2$$

The acidic character order is : $\boxed{\begin{array}{l} HCOOH > CH_3COOH > C_2H_5COOH \\ CCl_3COOH > HCCl_2COOH > CH_2Cl\,COOH > CH_3COOH \end{array}}$

Acidic character may be explained on the basis of I effect and resonance.

(b) Reaction with CH_2N_2 : Methyl ester can be prepared by this method.

$$RCOOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2$$

Methyl ester

8.3.2 Reaction due to – OH group

(a) Esterification :

$$CH_3CO\ OH + H\ O\ C_2H_5 \xrightarrow{Conc.H_2SO_4} CH_3COOC_2H_5 + H_2O$$

(b) Reaction with NH_3 :

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 \xrightarrow{P_2O_5/\Delta} CH_3CN$$

(c) Reaction with thionyl chloride :

$$CH_3COOH + SOCl_2 \xrightarrow{Pyridine} CH_3COCl + SO_2\uparrow + HCl$$

(d) Reaction with PCl_5 :

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

(e) Reaction with P_2O_5 (dehydrating agent) :

$$\begin{array}{l} CH_3CO\boxed{OH} \\ CH_3COO\boxed{H} \end{array} \xrightarrow[\text{conc. } H_2SO_4\ \Delta]{P_2O_5 \text{ or}} \begin{array}{l} CH_3CO \\ CH_3CO \end{array}\!\!\!> O + H_2O$$

HCOOH is dehydrated by Conc. H_2SO_4

$$HCOOH \xrightarrow{\text{Conc.}H_2SO_4} CO + [H_2O.H_2SO_4]$$

8.3.3 Reaction due to $-\overset{\overset{\displaystyle O}{\|}}{C}-$ group of COOH :

(a) $CH_3\!-\!COOH + 4H \xrightarrow{LiAlH_4} CH_3CH_2OH + H_2O$

(b) $R\!-\!COOH + 3H_2 \xrightarrow{Ni/\Delta} R\!-\!CH_2\!-\!OH + H_2O$

(c) $R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + 6HI \xrightarrow[\&\text{ high Pr}]{\text{Red P}} R\!-\!CH_3 + 2H_2O + 3I_2$

8.3.4 Reaction due to – COOH group :

(a) Decarboxylation :

$$\underset{\text{(soda lime)}}{CH_3COONa + NaOH / CaO} \xrightarrow{\Delta} CH_4 + Na_2CO_3$$

(b) Kolbe's electrolysis :

$$\begin{array}{l} CH_3COONa \\ CH_3COONa\text{ (aq.)} \end{array} \xrightarrow{\text{Electrolysis}} \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} + CO_2 + NaOH + H_2$$

(c) Hunsdiecker reaction :

$$CH_3COOAg + Br_2 \xrightarrow[h\nu]{CCl_4} CH_3Br + AgBr + CO_2$$

or Cl_2 or $CH_3Cl + AgCl + CO_2$

(d) Formation of carbonyl compounds :

$$\left.\begin{array}{l} (CH_3COO)_2Ca \xrightarrow{\Delta} CH_3COCH_3 \\ (HCOO)_2Ca \xrightarrow{\Delta} HCHO \end{array}\right] \rightarrow \text{Dry distillation}$$

$$\left.\begin{array}{l} 2HCOOH \xrightarrow{MnO} HCHO \\ 2CH_3COOH \xrightarrow{MnO} CH_3COCH_3 \end{array}\right] \rightarrow \text{Catalytic reduction}$$

(e) Schmidt reaction : The amine formed has one C - atom less than the reactant acid.

$$RCOOH + \underset{\text{Hydrazoic acid}}{N_3H} \xrightarrow[(2)H_2O]{(1)H_2SO_4} RNH_2 + CO_2 + N_2$$

8.3.5 Reaction due to alkyl (R) group :

(a) Halogenation [HVZ reaction] : Hell volhard Zelinsky reaction**] :** In this reaction α - H atoms are replaced by halogen atoms.

$$CH_3COOH + Cl_2 \xrightarrow{P} ClCH_2COOH \xrightarrow{P/Cl_2} Cl_2CHCOOH \xrightarrow{P/Cl_2} Cl_3CCOOH$$

GOLDEN KEY POINTS

Test for HCOOH and CH_3COOH

	Test	HCOOH	CH_3COOH
1.	Reducing character		
	Reducing agents -		
	Tollen reagent	Silver mirror	✘
	Fehling solution	Cu_2O red ppt.	✘
	$K_2Cr_2O_7$	Cr^{+3} (green)	✘
2.	Decarboxylation.	$Na_2CO_3 + H_2$	CH_4

Uses of Formic Acid :

(i) As an antiseptic

(ii) For preservation of fruits.

(iii) For leather tanning.

(iv) In dying wool and cotton fabrics.

Uses of Acetic Acid :

(i) Vinegar (6 - 10% solution) used as **table acid** and manufacture of pickles.

(ii) For manufacture of rubber from latex and casein from milk CH_3COOH is used as coagulant.

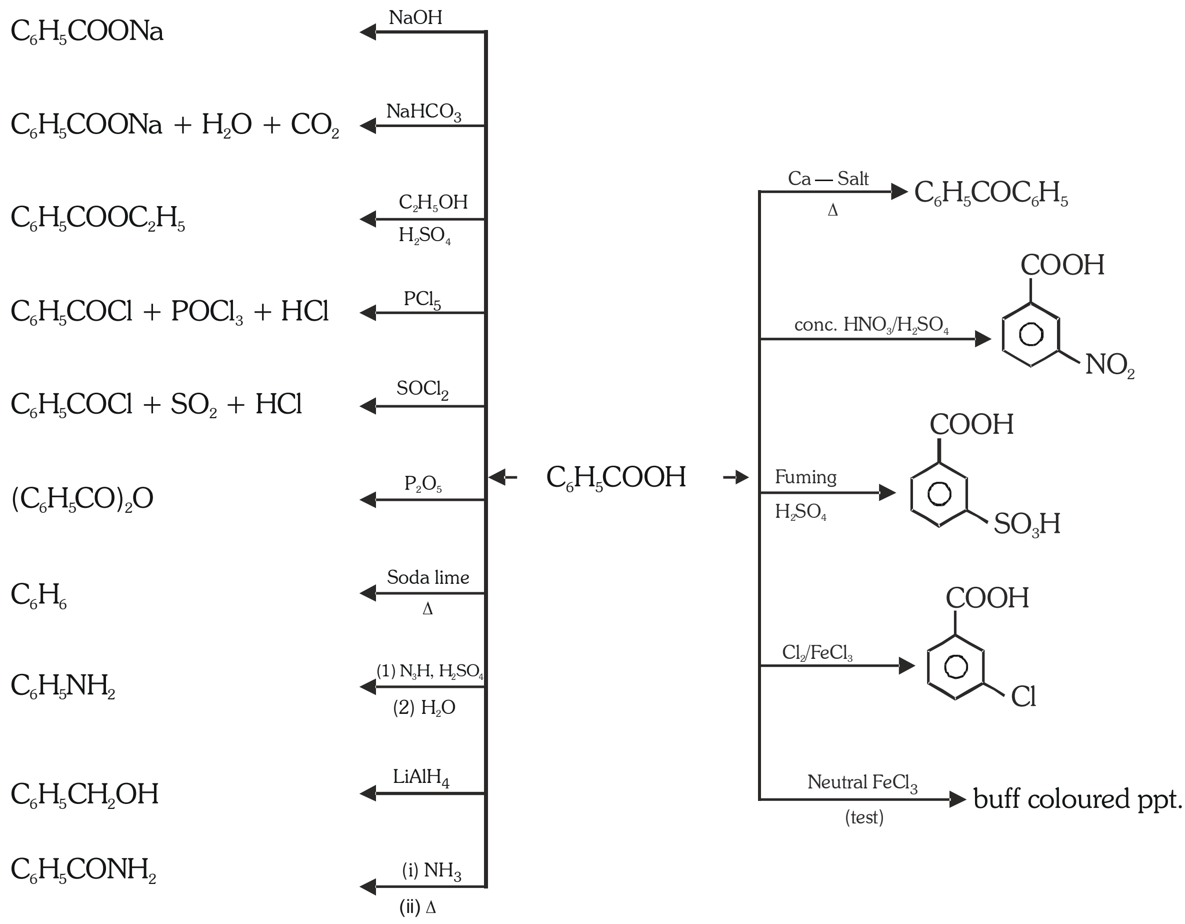
(iii) As a solvent and laboratory reagent.

9.0 BENZOIC ACID (C_6H_5COOH)

9.1 General Method of Preparation :

C_6H_5CHO	[O]	C_6H_5COOH
$C_6H_5CH_3$	$H^+/KMnO_4$	C_6H_5COOH
C_6H_5CN	H_3O^+	C_6H_5COOH
$C_6H_5CCl_3$	(i) aq. KOH (ii) $\overset{\oplus}{H}$	C_6H_5COOH
C_6H_5MgBr	(i) CO_2 (ii) H_2O	C_6H_5COOH
$H—O—C_6H_4COOH$ (o, m, p)	Zn, Δ	C_6H_5COOH
C_6H_5COCl	H_2O	C_6H_5COOH
C_6H_5COOR	H_2O	C_6H_5COOH

9.2 Chemical properties



10.0 ACID DERIVATIVES

Replacement of –OH group from a carboxylic group (– COOH) by a nucleophile like Cl^-, CH_3COO^-, $C_2H_5O^-$, NH_2^-, forms acid derivatives.

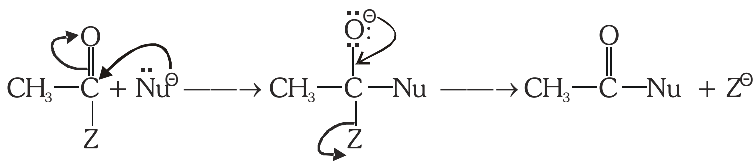
$$\underset{\text{Acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \xrightarrow[+Z]{-OH} \underset{\text{Acid derivative}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-Z}$$

$R-\overset{\overset{\displaystyle O}{\|}}{C}-$ is Acyl group and Z is nucleophile $Cl^{\ominus}$, $CH_3COO^{\ominus}$, $C_2H_5O^{\ominus}$, $NH_2^{\ominus}$

Ex. $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-$ Acetyl group

Characteristic reaction for acid derivatives is nucleophilic substitution reaction :

Mechanism :



In this reaction Z is leaving group. Weak bases are good leaving groups.

Reactivilty order : $\boxed{CH_3COCl > CH_3COOCOCH_3 > CH_3COOC_2H_5 > CH_3CONH_2}$

10.1 Acetyl Chloride

Replacement of —OH group from a —COOH group by Cl— atom gives acid chloride.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[+Cl]{-OH} R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl$$

10.1.1 General Method of Preparation :

(a) By heating CH_3COOH with PCl_3, PCl_5 & $SOCl_2$:

(i) $CH_3COOH + PCl_3 \longrightarrow CH_3COCl + H_3PO_3$

(ii) $CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$

(iii) $CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2\uparrow + HCl\uparrow$

(b) By heating the salt of acids with PCl_3, PCl_5 or $SOCl_2$:

(i) $CH_3COONa + PCl_3 \longrightarrow CH_3COCl + Na_3PO_3$

(ii) $CH_3COONa + PCl_5 \longrightarrow CH_3COCl + POCl_3 + NaCl$

(iii) $CH_3COONa + SOCl_2 \longrightarrow CH_3COCl + SO_2 + NaCl$

10.1.2 Physical properties :

(i) Pungent smelling liquid.

(ii) Boiling point 52°C.

(iii) Soluble in organic solvent, slowly soluble in water.

(iv) It produces fumes in moist air due to the formation of HCl.

10.1.3 Chemical properties :

(a) Hydrolysis : $CH_3CO\boxed{Cl + H}OH \longrightarrow CH_3COOH + HCl$

(b) Reaction with active H - contaning compounds (Acetylation) :

(i) $CH_3CO\boxed{Cl + H}NH_2 \longrightarrow CH_3CONH_2 + HCl$

(ii) $CH_3CO\boxed{Cl + H}NH-R \longrightarrow CH_3CONHR + HCl$

1° Amine — N– alkyl acetamide

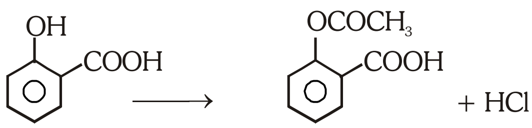
(iii) $CH_3CO\boxed{Cl + H}NR_2 \longrightarrow CH_3CONR_2 + HCl$

2° amine — N, N– dialkyl acetamide

(iv) $CH_3CO\boxed{Cl + H}OR \longrightarrow CH_3COOR + HCl$

Alcohol — Alkyl acetate

(v) CH_3COCl +

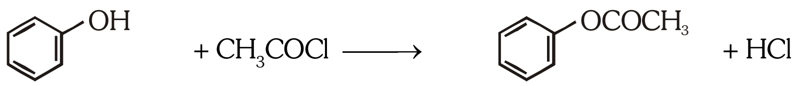


Salicylic acid — Aspirin (Acetyl salicylic acid)

(vi) $CH_3-\overset{\overset{O}{\|}}{C}-\boxed{Cl + H}-NH-NH_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NHNH_2 + HCl$

Acetyl hydrazide

$$\left[\underset{\text{Ketone}}{R-\overset{\overset{O}{\|}}{C}-R} + NH_2NH_2 \longrightarrow \underset{\text{hydrazone}}{R_2C{=}NNH_2}\right]$$

(vii) 

(Phenyl acetate)

(c) Reduction :

(i) $CH_3COCl + H_2 \xrightarrow{Pd/BaSO_4} CH_3CHO$ (Rosenmund's reduction)

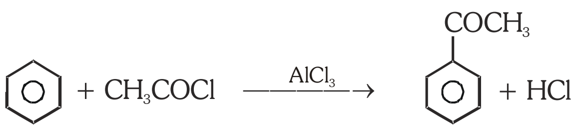
(ii) $CH_3COCl + 4H \xrightarrow[(2)H_2O]{(1)LiAlH_4} CH_3CH_2OH + HCl$

(d) With Sodium acetate : $CH_3CO\boxed{Cl + Na}O-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3CO-O-\overset{\overset{O}{\|}}{C}-CH_3 + NaCl$

Acetic anhydride

(e) With Sodium ethoxide : $CH_3CO\boxed{Cl + Na}OC_2H_5 \longrightarrow CH_3COOC_2H_5 + NaCl$

Ethyl acetate

(f) Friedel crafts reaction : 

Acetophenone

10.2 Acetic Anhydride (Ethanoic Anhydride)

10.2.1 General Method of Preparation :

(a) By heating acetyl Chloride with anhydrous sodium acetate [Lab. Method] :

$$CH_3CO\boxed{Cl + Na}O-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{\Delta} CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + NaCl$$

(b) By Dehydration of acetic acid :

$$\underset{\text{Acetic acid}}{2CH_3COOH} \xrightarrow[\text{dehydration}]{P_2O_5} \underset{\text{acetic anhydride}}{(CH_3CO)_2O} + H_2O$$

10.2.2 Physical Properties :

(i) It is pungent smelling liquid.

(ii) Sparingly soluble in water, soluble in ether & alcohol.

(iii) Boiling point 139°C.

10.2.3 Chemical Properties :

(a) Hydrolysis :

$$CH_3CO-O\overset{H\,|\,OH}{|}COCH_3 \longrightarrow CH_3COOH + CH_3COOH$$

Hydrolysis order : $\boxed{\textbf{Alkaline > Acidic > neutral}}$

$$CH_3CO{-}O\overset{\overset{+}{Na}\,|\,\overset{-}{O}H}{|}COCH_3 \longrightarrow \underset{\text{sodium acetate}}{CH_3COONa} + \underset{\text{Acetic acid}}{CH_3COOH}$$

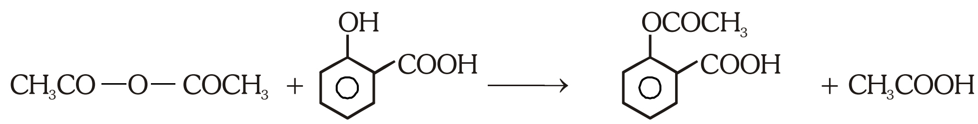
(b) Reaction with active H - containing compounds (Acetylation) :

(i) $CH_3-CO-\boxed{OCOCH_3 + H}NH_2 \longrightarrow CH_3CONH_2 + CH_3COOH$

(ii) $CH_3CO-\boxed{OCOCH_3 + H}NHR \longrightarrow CH_3CONHR + CH_3COOH$

(iii) $CH_3CO-\boxed{O-COCH_3 + H}NR_2 \longrightarrow CH_3CONR_2 + CH_3COOH$

(iv) $CH_3CO-\boxed{O-COCH_3 + H}OR \longrightarrow CH_3COOR + CH_3COOH$

(v) 

(Salicylic acid) (Aspirin)

(c) Reduction : With $LiAlH_4$ in ether gives ethyl alcohol

$$CH_3CO-O-COCH_3 \xrightarrow{LiAlH_4} 2CH_3CH_2OH + H_2O$$

(d) Reaction with PCl_5 & $SOCl_2$:

$$\begin{array}{l} CH_3CO\,|{-}O{-}|\,COCH_3 \\ \quad\;\; Cl\,|{-}PCl_3{-}|\,Cl \end{array} \longrightarrow 2CH_3COCl + \underset{\text{Phosphorous Oxychloride}}{POCl_3}$$

$$\begin{array}{l} CH_3CO\,|{-}O{-}|\,COCH_3 \\ \quad\;\;\; Cl\,|{-}SO{-}|\,Cl \end{array} \longrightarrow 2CH_3COCl + SO_2$$

10.2.4 Uses

(i) As an acetylating agent

(ii) In the manufacture of cellulose acetate, aspirin, phenacetin, acetamide, & acetophenone etc.

(iii) For detection and estimation of hydroxyl and amino group.

10.3 Ethyl acetate

10.3.1 General Method of Preparation :

(a) Tischenko reaction : By treating acetaldehyde with aluminium ethoxide. (Modified cannizaro reaction)

$$2CH_3CHO \xrightarrow{(C_2H_5O)_3Al} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

(b) Esterification :

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + HO-C_2H_5 \underset{\Delta}{\overset{Conc.H_2SO_4}{\rightleftharpoons}} \underset{\text{Ethylacetate}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5} + H_2O$$

BEGINNER'S BOX-6

1. Alkanoic acids can be prepared by hydrolysis of:-

(1) Trihaloalkanes (2) 1,1,1–trihaloalkanes

(3) Grignard reagents (4) Ketones

2. Acids have much higher boiling points than isomeric esters because :-

(1) Acids form dimers by H–Bonding

(2) Acids are volatile in steam

(3) Esters are non–volatile

(4) Acids can ionise to give protons in aqueous solution

3. Which of the following compounds can form intermolecular H–bonds :-

(1) Ethyl acetate (2) Methyl formate

(3) Acetamide (4) Acetic anhydride

4. Reaction of ethyl acetate with sodium ethoxide gives acetoacetic ester. This reaction is known with the name of :-

(1) Claisen (2) Clemmensen

(3) Cannizaro (4) Etard

10.3.2 Physical Properties

(i) Fruity smell liquid.

(ii) Boling point 77°C.

(iii) Slightly soluble in water, soluble in organic solvent.

10.3.3 Chemical Properties :

(a) Hydrolysis : In acidic medium reaction is reversible and in alkaline medium reaction is irreversible.

$$CH_3COOC_2H_5 + HOH \xrightleftharpoons{H^+} CH_3COOH + C_2H_5OH$$

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

(b) Ammonolysis : $CH_3CO\boxed{OC_2H_5 + H}NH_2 \xrightarrow{\Delta} CH_3CONH_2 + C_2H_5OH$

Acetamide Ethanol

(c) Reaction with NH_2NH_2 & NH_2OH :

$$CH_3CO\boxed{OC_2H_5 + H}NHNH_2 \xrightarrow{\Delta} CH_3CONHNH_2 + C_2H_5OH$$

Hydrazine Acetyl hydrazide

$$CH_3CO\boxed{OC_2H_5 + H}NHOH \xrightarrow{\Delta} CH_3CONHOH + C_2H_5OH$$

hydroxyl amine Acetyl hydroxamic acid

(d) Reduction : $CH_3COOC_2H_5 \xrightarrow{LiAlH_4} CH_3CH_2OH + C_2H_5OH$

(e) Claisen condensation :

$$CH_3CO\boxed{OC_2H_5 \ + H}CH_2COOC_2H_5 \xrightarrow{NaOC_2H_5} CH_3COCH_2COOC_2H_5 + C_2H_5OH$$

10.4 Acetamide

10.4.1 General Method of Preparation :

(a) Ammonolysis of acid derivatives :

$$CH_3CO\boxed{Cl + H}NH_2 \longrightarrow CH_3CONH_2 + HCl$$

$$CH_3CO\boxed{-O-COCH_3 + H}NH_2 \longrightarrow CH_3CONH_2 + CH_3COOH$$

$$CH_3CO\boxed{OC_2H_5 + H}NH_2 \xrightarrow{\Delta} CH_3CONH_2 + C_2H_5OH$$

(b) Hydrolysis of alkyl cyanides : By the partial hydrolysis of alkyl cyanides.

$$R-C\equiv N + H_2O \longrightarrow R-\underset{\underset{O}{\|}}{C}-NH_2$$

$$CH_3-C\equiv N + H_2O \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-NH_2$$

10.4.2 Physical Properties :

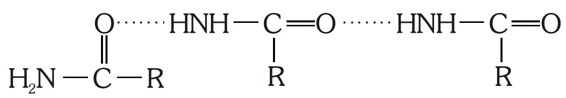
(i) Acetamide is white crystalline solid.

(ii) Pure acetamide is odourless.

(iii) Impure acetamide - Smell like mouse.

(iv) Lower amides are soluble in water, due to H–bonding.

(v) Their higher M. P. and B. P. are due to intermolecular H– bonding.



10.4.3 Chemical Properties :

(a) Hydrolysis : Amides are hydrolysed rapidly in acidic medium. In alkaline medium hydrolysis is carried out in temperature condition.

$$R-\underset{\underset{O}{\|}}{C}-NH_2 + H_2O \xrightarrow{H^+} R-COOH + \overset{+}{N}H_4$$

$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 + NaOH \xrightarrow{\Delta} CH_3COONa + NH_3\uparrow$$

(b) Reduction to primary amines : Amine contains same number of carbon atoms.

$$CH_3CONH_2 \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} \underset{1^\circ \text{ amine}}{CH_3CH_2NH_2} + H_2O$$

(c) Dehydration with PCl_5, $SOCl_2$ or P_2O_5 :

$$CH_3CONH_2 \xrightarrow{PCl_5} CH_3CCl_2NH_2 \xrightarrow{-2HCl} \underset{\text{Methyl cyanide}}{CH_3CN} + 2HCl$$

$$CH_3CONH_2 + P_2O_5 \xrightarrow{\Delta} \underset{\text{Methyl cyanide}}{CH_3CN} + H_2O$$

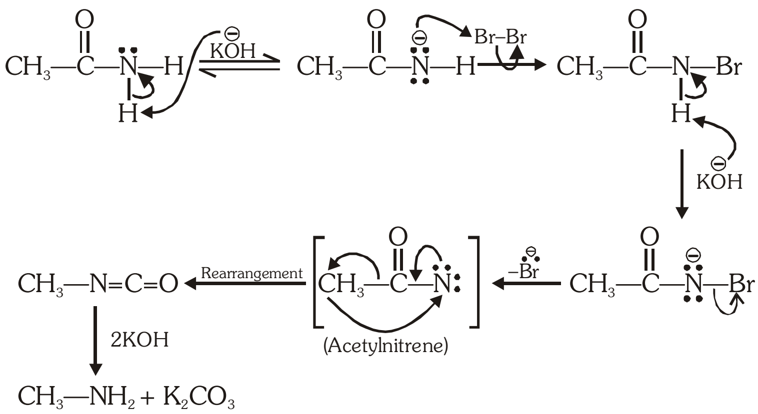
(d) Reaction with nitrous acid :

$$\begin{array}{l} CH_3-CO-N\,H_2 \\ \quad\;\; HO-N-O \end{array} \xrightarrow{HNO_2} CH_3COOH + N_2 + H_2O$$

(e) Hoffmann's bromamide degradation reaction : Amides on reaction with bromine, and NaOH or KOH yield primary amines, having one C–atom less than the amides.

$$\underset{\text{or (KOBr)}}{CH_3CONH_2 + Br_2 + KOH(aq.)} \longrightarrow CH_3NH_2 + KBr + K_2CO_3 + H_2O$$

Mechanism :



ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3								
	Ans.	3	4	2								

BEGINNER'S BOX-2	Que.	1	2									
	Ans.	1	2									

BEGINNER'S BOX-3	Que.	1	2	3								
	Ans.	3	2	3								

BEGINNER'S BOX-4	Que.	1	2	3								
	Ans.	2	4	1								

BEGINNER'S BOX-5	Que.	1	2	3								
	Ans.	4	2	3								

BEGINNER'S BOX-6	Que.	1	2	3	4							
	Ans.	2	1	3	1							

EXERCISE-I (Conceptual Questions)

ALCOHOL

1. The compound A, B and C in the reaction sequence

$$CH_3CH_2OH \xrightarrow{PBr_3} A \xrightarrow[\Delta]{alc.KOH} B \xrightarrow{Br_2} C$$

are given by the set

(1) C_2H_5Br, CH_3CH_2OH, CH_3CHBr_2.

(2) C_2H_5Br, $CH{\equiv}CH$, $CH_2{=}CHBr$

(3) C_2H_5Br, $CH_2{=}CH_2$, $CH_2Br{-}CH_2Br$

(4) C_2H_5Br, CH_3CH_2OH, $BrCH_2{-}CH_2Br$

2. Primary amines can be converted into alkanols by reaction with

(1) Aqueous HCl (2) Tilden's reagent

(3) $NaNO_2$ and dil. HCl (4) Hypochlorous acid

3. Which of the following alcohols gives a red colour in Victor Meyer test

(1) $CH_3{-}CH_2{-}CH_2{-}OH$ (2) $CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}OH$

(3) $(CH_3)_3C{-}OH$ (4) $CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_2{-}CH_3$

4. Methanol on heating with salicylic acid and a few drops of conc. H_2SO_4 gives the smell of

(1) Bitter almonds (2) Oil of wintergreen

(3) Rotten eggs (4) Mustard oil

5. Which of the following does not turn orange colour of chromic acid to green

(1) 1° alcohol (2) 2° alcohol

(3) 3° alcohol (4) Allyl alcohol

6. p, s and t-alcohols can be distinguished by :-

(1) Reimer-Tiemann reaction

(2) Tollen's reagent

(3) Lucas test

(4) Lassaigne's test

7. Consider the following reaction :

$C_2H_5OH + H_2SO_4 \rightarrow$ Product

Among the following, which one cannot be formed as a product under any conditions ?

(1) $C_2H_5OSO_3H$

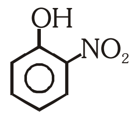
(2) $H_2C{=}CH_2$

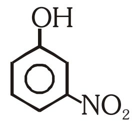
(3) $HC{\equiv}CH$

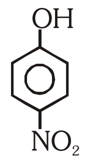
(4) $CH_3{-}CH_2{-}O{-}CH_2{-}CH_3$

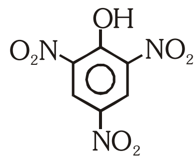
PHENOL

8. Nitration of phenol with conc. nitric acid gives :-

(1) 

(2) 

(3) 

(4) 

9. Deoxygenation of phenol can be achieved by distillation with :-

(1) Raney nickel

(2) Lithium aluminium hydride

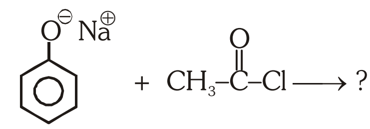
(3) Sodium borohydride

(4) Zinc dust

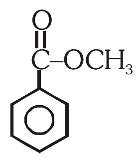
10. Which of the following compounds shows intramolecular hydrogen bonding :-

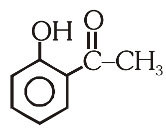
(1) p–Nitrophenol (2) Ethanol

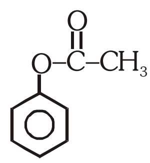
(3) o–Nitrophenol (4) Methanamine

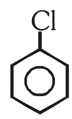
11. 

Sodium phenate

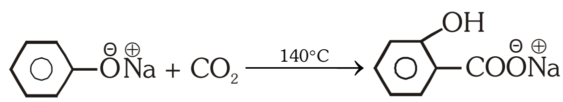
(1) 

(2) 

(3) 

(4) 

12. The reaction



is called :-

(1) Schotten Bauman reaction

(2) Kolbe Schmidt reaction

(3) Reimer–Tiemann reaction

(4) Lederer–Manasse reaction

13. Phenol can be distinguished from ethanol by reactions with the following except :-

(1) Iodine and alkali (2) Ferric chloride

(3) Acetyl chloride (4) Bromine water

14. Phenol on treatment with methyl chloride in the presence of anhydrous $AlCl_3$ gives chiefly :-

(1) o–cresol (2) m–cresol

(3) anisole (4) p–cresol

15. Phenol on heating with $NaNO_2$ and a few drops of conc. H_2SO_4 mainly gives :-

(1) p–nitrophenol (2) p–nitrosophenol

(3) o–nitrophenol (4) m–nitrosophenol

16. Phenol and benzoic acid are distinguished by :-

(1) Lucas reagent (2) Victor Meyer test

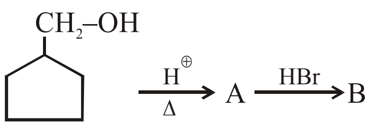
(3) Caustic soda (4) Sodium bicarbonate

17. Phenol can be distinguished from ethanol by the reaction with

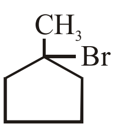
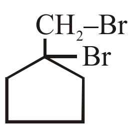
(1) Na (2) Br_2/Water

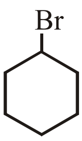
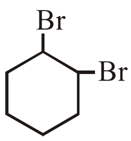
(3) Neutral $AlCl_3$ (4) 1 and 2 Both

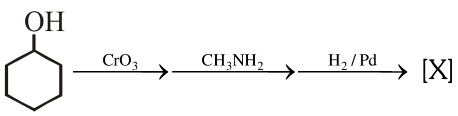
ETHER

18. 

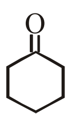
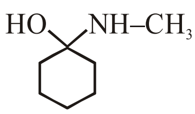
What is the structure of B :-

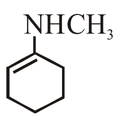
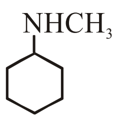
(1)  (2) 

(3)  (4) 

19. 

Product [X] of given reaction is :-

(1)  (2) 

(3)  (4) 

20. $CH_3-\underset{OH}{\underset{|}{C}H}-CH_3 \xrightarrow{PBr_3} X \xrightarrow{Mg/ether} Y \xrightarrow{H_2O/H^+}$

The final product is :-

(1) $CH_3-\underset{CH_3}{\underset{|}{C}H}-OH$

(2) $CH_3-CH_2-CH_2-OH$

(3) $CH_3-\underset{CH_3}{\underset{|}{C}H}-O-\underset{CH_3}{\underset{|}{C}H}-CH_3$

(4) $CH_3-CH_2-CH_3$

21. In the reaction sequence

$A \xrightarrow{HBr} B \xrightarrow{C_2H_5ONa}$ Ethoxyethane,

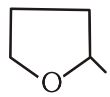
A and B are :-

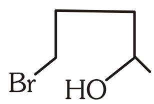
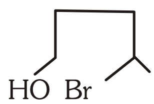
(1) C_2H_6, C_2H_5Br

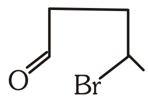
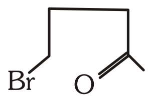
(2) CH_4, CH_3Br

(3) $CH_2=CH_2$, C_2H_5Br

(4) $CH\equiv CH, CH_2=CHBr$

22.  + H–Br ?

(1)  (2) 

(3)  (4) 

23. $CH_3-CH_2-OH + Ph-CH_2-OH \xrightarrow[140°C]{H^{\oplus}}$ of which is not obtained?

(1) $CH_3-CH_2-OCH_2-CH_3$

(2) $Ph-CH_2-OCH_2-Ph$

(3) $Ph-CH_2-O-CH_2-CH_3$

(4) $Ph-CH_2-O-CH_2-O-CH_3$

24. Oxonium ion of ether has the structure :-

(1) $C_2H_5-O-\underset{CH_3}{\underset{|}{C}H}-\underset{H}{\underset{|}{O^{\oplus}}}-H$

(2) $CH_3-CH_2-\underset{H}{\underset{|}{O^{\oplus}}}-CH_2-CH_3$

(3) $(C_2H_5)_2O \rightarrow O$

(4) $CH_3-CH_2-O-CH_2-CH_2-\underset{H}{\underset{|}{O^{\oplus}}}-O-H$

25. What will happen when diethyl ether treated with hot and conc. HI :–
(1) Ethyl alcohol (2) Ethyl iodide
(3) Methyl iodide (4) Methanol

26. Which of the following does not react with aq. NaOH :-
(1) Phenol (2) Benzoic acid
(3) CH_3COOH (4) $CH_3-O-C_6H_5$

CARBONYL COMPOUNDS

27. Acetaldehyde on warming with Fehling's solution gives a red precipitate of :-
(1) Elemental copper
(2) Cuprous oxide
(3) Cupric oxide
(4) Mixture of all of the above

28. Acetone does not form :-
(1) A phenylhydrazone with phenylhydrazine
(2) A sodium bisulphite adduct with sodium bisulphite
(3) A silver mirror with Tollen's reagent
(4) An oxime with hydroxylamine

29. CH_3CHO and CH_3COCH_3 can not be distinguished by :-
(1) Fehling solution (2) Grignard reagent
(3) Schiff's reagent (4) Tollen's reagent

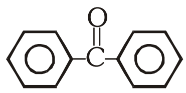
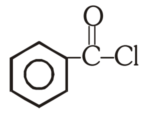
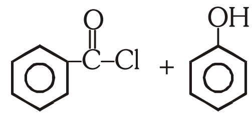
30. In the reaction

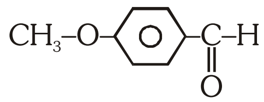
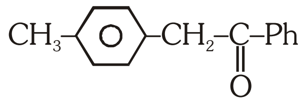
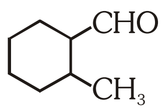
$$CH_3CH_2COOH \xrightarrow[(2)\ Br_2/CCl_4]{(1)\ \text{moist } Ag_2O,\ \Delta} A \xrightarrow[\text{Ether}]{Mg} B \xrightarrow{CH_3CN/H_3O^{\oplus}} C$$

The product C is -
(1) $CH_3CH_2-CH(OH)-CH_3$
(2) CH_3CH_2-CN
(3) $CH_3CH_2-C(=O)-CH_3$
(4) $CH_3-CH_2-CH(COOH)-CH_3$

31. Acetone is obtained by the hydrolysis of the addition product of methyl magnesium iodide and :-
(1) HCHO (2) CH_3CHO
(3) CH_3COCH_3 (4) $CH_3-C\equiv N$

32. $Ph-CCl_2-CH_3$ + aq. KOH $\rightarrow$ A $\xrightarrow[H^{\oplus}]{KCN}$ B ?
(1) 50% d + 50% ℓ (2) 80% d + 20% ℓ
(3) Meso compound (4) optically active

33.  can be obtained by :-
(1)  + $(Ph)_2Cd$
(2) 
(3)  + CO + $ZnCl_2$ + HCN
(4) None of the above

34. Which does not react with $NaHSO_3$.
(1) $Ph-C(=O)-H$
(2) 
(3) 
(4) 

35. Ketones can be prepared by :-
(1) Rosenmund reduction
(2) Etard reaction
(3) Cannizzaro reaction
(4) Friedel-Craft reaction

36. Carbonyl compounds are best purified by :-
(1) Steam distillation
(2) Hydrolysis of sodium bisulphite adducts
(3) Fractional crytallisation
(4) Sublimation

37. Carbonyl compounds readily undergo :-
(1) Nucleophilic substitutions
(2) Electrophilic addition reactions
(3) Nucleophilic addition reactions
(4) Free radical substitution reactions

38. $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ and $CH_3-\overset{O}{\overset{\|}{C}}-H$ are readily distinguished by their reaction with :-
(1) Iodine and alkali
(2) 2,4-dinitrophenylhydrazine
(3) Tollen's reagent
(4) All the above

39. Formaldehyde and acetaldehyde are readily distinguished by reaction with :-
(1) A solution of 2,4-dinitrophenylhydrazine
(2) Fehling's solution
(3) Tollen's reagent
(4) Iodine and alkali

40. Which is the most suitable reagent for the following conversion

$$CH_3-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

(1) $\xrightarrow[\text{(ii)}H^{\oplus}]{\text{(i)Tollen's reagent}}$ (2) $\xrightarrow[\text{(ii)}H^{\oplus}]{\text{(i)Benzoyal peroxide}}$

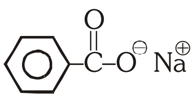
(3) $\xrightarrow[\text{(ii)}H^{\oplus}]{\text{(i)}I_2 \text{ and NaOH}}$ (4) $\xrightarrow{KMnO_4/H^{\oplus},\ \Delta}$

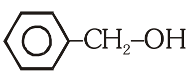
41. Formaldehyde reacts with conc. alkali to form :-
(1) A resinous mass
(2) Formic acid
(3) A mixture of methanol and sodium formate
(4) Methanol

42. Which of the following compounds does not give aldol condensation :-
(1) CH_3CHO (2) CH_3CH_2CHO
(3) HCHO (4) $CH_3CH_2CH_2CHO$

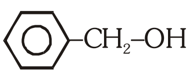
43. Cannizzaro reaction is given by :-
(1) Aldehydes containing α-hydrogen atoms
(2) Aldehydes as well as ketones containing α-hydrogen atoms
(3) Aldehydes not containing α-hydrogen atoms
(4) Aldehydes containing β-hydrogen atoms

44. Benzaldehyde reacts with formaldehyde in the presence of alkali to form :-

(1) CH_3-OH and 

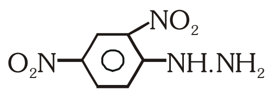
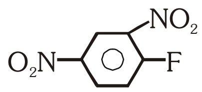
(2)  and $H-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\ \overset{\oplus}{Na}$

(3) 

(4) $H-\overset{O}{\overset{\|}{C}}-OH$ and 

45. Which of the following can be converted to $CH_3-CH=CH-CHO$:-
(1) Acetone (2) Acetaldehyde
(3) Propanaldehyde (4) Formaldehyde

46. The product of reaction with primary amine and aldehyde is -
(1) $R-\overset{O}{\overset{\|}{C}}-OH$ (2) R–ONO
(3) R'–CH=N–R (4) $R-NO_2$

47. Brady's reagent is
(1) $[Cu(NH_3)_4]SO_4$
(2) $KMnO_4/NaIO_4$
(3) 
(4) 

48. A compound with molecular formula C_3H_6O, not gives silver mirror with Tollen's reagent but forms oxime with hydroxyl amine. Compound will be -
(1) $CH_2{=}CH{-}CH_2{-}OH$
(2) CH_3CH_2CHO
(3) $CH_2{=}CH{-}O{-}CH_3$
(4) CH_3COCH_3

49. Aldehyde and ketone are distinguished by reagent
(1) Fehling solution (2) H_2SO_4
(3) $NaHSO_3$ (4) NH_3

50. Carbonyl group is converted into methylene group by -
(1) Acidic reduction
(2) Raney Ni
(3) Basic hydrolysis
(4) Normal Hydrogenation

51. When acetaldol is treated with excess of acid then unsaturated product will be :-
(1) Alcohol (2) Aldehyde
(3) Acid (4) Alkyl halide

52. The reagent used for the separation of acetaldehyde from acetophenone is -
(1) $NaHSO_3$ (2) $C_6H_5NHNH_2$
(3) NH_2OH (4) NaOH + I_2

53. The most suitable reagent for the conversion of $RCH_2OH \longrightarrow RCHO$

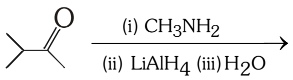
(1) $KMnO_4$

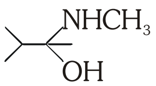
(2) $K_2Cr_2O_7$

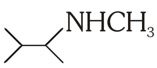
(3) CrO_3

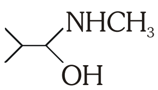
(4) PCC (Pyridinium chloro chromate)

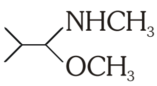
54. The major organic product formed from the following reaction is :–



(1) 

(2) 

(3) 

(4) 

55. $\underset{H}{\overset{Me}{>}}C = O + H_2N - \overset{O}{\overset{\|}{C}} - NH - NH_2 \xrightarrow{H^{\oplus}}$

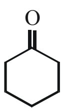
which is incorrect :-

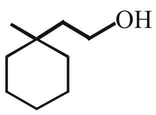
(1) The reaction completes through addition elimination mechanism.

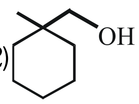
(2) $\underset{H}{\overset{Me}{>}}C = N - \overset{O}{\overset{\|}{C}} - NH - NH_2$ is formed as product

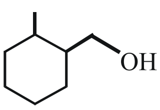
(3) The reaction is an example of condensation reaction

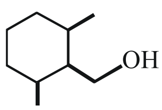
(4) None

56.  $+ CH_3MgBr \xrightarrow{H^{\oplus}/H_2O} P \xrightarrow{HBr} Q \xrightarrow[Ether]{Mg} R \xrightarrow[H^{\oplus}/H_2O]{HCHO} S$, S is:

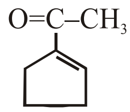
(1) 

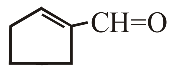
(2) 

(3) 

(4) 

57. $H-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\overset{\ominus}{OH}/\Delta}$ Product (A) is :-

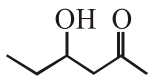
(1) 

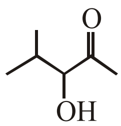
(2) 

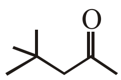
(3) $\underset{OH}{\underset{|}{CH_2}}-CH_2CH_2CH_2CH_2-COOH$

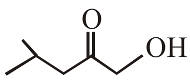
(4) $\underset{OH}{\underset{|}{CH_2}}-CH_2CH_2CH_2CH_2-\underset{OH}{\underset{|}{CH_2}}$

58. Which of the following compounds is the product of an aldol reaction :-

(1) 

(2) 

(3) 

(4) 

59. Which product is obtained by aldol reaction :-

(1) α – Hydroxy aldehyde or ketone

(2) β – Hydroxy aldehyde or ketone

(3) α,β – unsaturated ester

(4) β – Hydroxy acid

CARBOXYLIC ACID

60. When propanoic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The C of CO_2 comes from :-

(1) methyl group

(2) carboxylic acid group

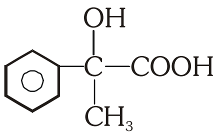
(3) methylene group

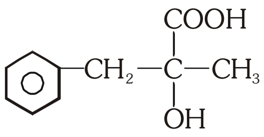
(4) bicarbonate

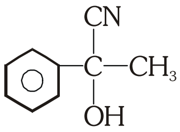
61. In a set of reactions acetic acid yielded a product D

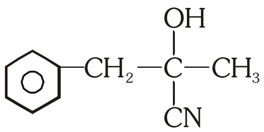
$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow[\text{Anhy. } AlCl_3]{\text{Benzene}} B \xrightarrow{HCN} C \xrightarrow{H_3O^{\oplus}} D$

The structure of D would be –

(1) 

(2) 

(3) 

(4) 

ACID DERIVATIVE

62. The compounds A and B in the reaction sequence

$B \xleftarrow{\text{Phenol}} CH_3COCl \xrightarrow{CH_3COONa} A$

are given by the set :-

(1) $CH_3CO–O–COCH_3$, $C_6H_5CH_2OH$

(2) $CH_3CO–O–COCH_3$, $C_6H_5OCOCH_3$

(3) CH_3COCH_3, $C_6H_5OCOCH_3$

(4) $CH_3-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-CH_3$, $CH_3-\underset{\underset{O}{\|}}{C}-O-C_6H_5$

63. $CH_3–CH_2–COOH \xrightarrow{P/Cl_2} A \xrightarrow[KOH]{Alc.} B$

structure of B is :-

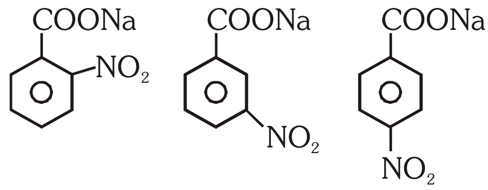
(1) $CH_2=CH–COOH$

(2) $CH_3–\underset{\underset{Cl}{|}}{CH}–COOH$

(3) $\underset{\underset{Cl}{|}}{CH_2}–CH_2–COOH$

(4) $CH_3–CH_2–\overset{\overset{O}{\|}}{C}–Cl$

64. Correct reactivity order of decarboxylation is

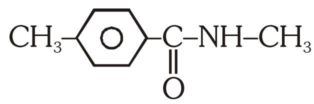


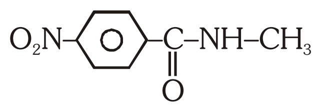
I II III

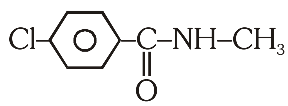
(1) I > II > III (2) I > III > II

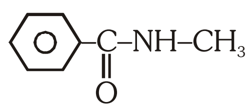
(3) III > II > I (4) III > I > II

65. Which is most reactive towards hydrolysies.

(1) 

(2) 

(3) 

(4) 

66. Which of the following reagents may be used to distinguish between phenol and benzoic acid ?

(1) Victor-Mayer test

(2) Neutral $FeCl_3$

(3) Aqueous NaOH

(4) Tollen's reagent

67. Acyl chlorides undergo :-

(1) Nucleophilic addition reactions

(2) Nucleophilic substitution reactions

(3) Electrophilic substitution reactions

(4) Electrophilic addition reactions

68. The reaction of ethanol on acetic anhydride is an example of :-

(1) Nucleophilic addition

(2) Nucleophilic substitution

(3) Electrophilic addition

(4) Free radical substitution

69. The reduction of acetamide gives :-

(1) $CH_3CH_2NH_2$

(2) $(CH_3)_2CHNH_2$

(3) $(CH_3)_3CNH_2$

(4) $(CH_3CH_2)_2NH$

70. Which is used in preparation of aldehyde by rosenmund reduction

(1) Ester (2) Acid

(3) Acid halide (4) Alcohol

71. Which is maximum reactive :-

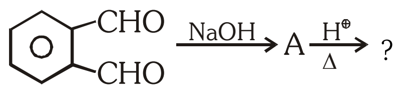
(1) CH_3CONH_2 (2) CH_3COOCH_3

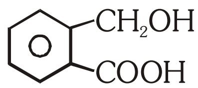
(3) CH_3COCl (4) $CH_3COOC_2H_5$

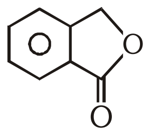
72. $CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[\Delta]{P_2O_5} ?$

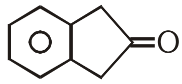
(1) CH_3COOH (2) CH_3-CN

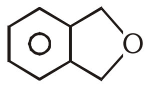
(3) CH_3-CH_3 (4) CH_3-CHO

73. 

(1) 

(2) 

(3) 

(4) 

EXERCISE-I (Conceptual Questions) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	3	1	2	3	3	3	4	4	3	3	2	3	4	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	4	2	3	4	4	3	1	4	2	2	4	2	3	2	3
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	4	1	1	3	4	2	3	3	4	3	3	3	3	2	2
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	3	3	4	1	1	2	1	4	2	2	2	2	1	2	4
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73		
Ans.	1	2	1	1	2	2	2	2	1	3	3	2	2		

EXERCISE-II (Assertion & Reason)

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

(A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.

(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.

(C) If Assertion is True but the Reason is False.

(D) If both Assertion & Reason are false.

1. ***Assertion :–*** Chlorobenzene and benzyl chloride can be distinguished by treatment with $AgNO_3$.
Reason :– Chlorobenzene does not gives white ppt with $AgNO_3$ due to resonance.
(1) A (2) B (3) C (4) D

2. ***Assertion :–*** Benzyl alcohol turns blue litmus red.
Reason :– Benzyl alcohol is not an isomer of p-cresol.
(1) A (2) B (3) C (4) D

3. ***Assertion :–*** Phenol is stronger acid than alcohols.
Reason :– Phenol is stabilized by resonance whereas alcohol are not.
(1) A (2) B (3) C (4) D

4. ***Assertion :–*** Addition of CH_3OH to phenyl magnesium bromide gives benzene.
Reason :– CH_3OH is a stronger acid than benzene.
(1) A (2) B (3) C (4) D

5. ***Assertion :–*** Ethers behave as bases in the presence of mineral acids.
Reason :– Ethers have lone pairs of electrons on oxygen.
(1) A (2) B (3) C (4) D

6. ***Assertion :–*** Phenols give o- and p-Nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.
Reason :– –OH group in phenol shows –M effect.
(1) A (2) B (3) C (4) D

7. ***Assertion :–*** Formic acid is a stronger acid than benzoic acid.
Reason :– pK_a of formic acid is higher than that of benzoic acid.
(1) A (2) B (3) C (4) D

8. ***Assertion :–*** Ketones on reaction with grignard reagents, followed by hydrolysis yield tertiary alcohols.
Reason :– All ketones show haloform reaction.
(1) A (2) B (3) C (4) D

9. ***Assertion :–*** >C=O group is present both in aldehydes and acid derivatives.
Reason :– Aldehyde give nucleophilic addition across >C=O bond but acid derivatives do not exhibit such reactions.
(1) A (2) B (3) C (4) D

10. ***Assertion :–*** Benzamide and methyl benzoate are derivatives of benzoic acid.
Reason :– Benzamide is less easily hydrolysed as compared to methyl benzoate.
(1) A (2) B (3) C (4) D

11. ***Assertion :-*** Dehydration of alcohols always takes place in basic medium.
Reason :- OH^- is a good leaving group
(1) A (2) B (3) C (4) D

12. ***Assertion :-*** Acetamide on reaction with KOH and bromine gives acetic acid.
Reason :- Bromine catalyses hydrolysis of acetamide.
(1) A (2) B (3) C (4) D

13. ***Assertion :-*** Mixture of benzaldehyde and acetaldehyde in hot alkaline medium gives cinnamaldehyde.
Reason :- Benzaldehyde is strong electrophile than acetaldehyde.
(1) A (2) B (3) C (4) D

14. ***Assertion :-*** Acetophenone shows aldol condensation.

Reason :- Acetophenone contains carbonyl group.

(1) A (2) B (3) C (4) D

15. ***Assertion :*** Benzyl phenyl ether forms phenol and benzyl iodide with HI

Reason : Because benzyl carbocations is more stable than phenyl carbocation.

(1) A (2) B (3) C (4) D

16. ***Assertion :-*** m-Nitrophenol is less acidic than p-nitrophenol.

Reason :- p-Nitrophenol has intermolecular-H-bonding.

(1) A (2) B (3) C (4) D

17. ***Assertion :-*** Benzene sulphonic acid on heating with NaOH gives phenoxide.

Reason :- Sulphonic group is a poor leaving group.

(1) A (2) B (3) C (4) D

18. ***Assertion :-*** Acetamide on reaction with Br_2/NaOH give CH_3–NH_2.

Reason :- Carbon of amide functional group becomes part of Na_2CO_3.

(1) A (2) B (3) C (4) D

19. ***Assertion :-*** Ph–O–C_2H_5 can be prepared form PhONa and ethyl iodide.

Reason :- Aryl halides are less reactive substrates for nucleophilic substitution reaction.

(1) A (2) B (3) C (4) D

20. ***Assertion :-*** $C_6H_5CH(OH)CH_3$ gives benzoic acid with NaOBr followed by hydrolysis.

Reason :- First dehydration occur then oxidation

(1) A (2) B (3) C (4) D

21. ***Assertion :-*** Ethyl acetoacetate forms butane-1,4-diol with $NaBH_4$.

Reason :- $NaBH_4$ can reduces ketone and esters group.

(1) A (2) B (3) C (4) D

22. ***Assertion :-*** Methoxy ethane has less boiling point than propanol.

Reason :- Methoxy ethane is more polar than propanol.

(1) A (2) B (3) C (4) D

23. ***Assertion :-*** Isopropyl benzene reacts with O_2 and acid gives phenol.

Reason :- Initially isoproyl benzene converts into 2-phenyl propan-2-ol.

(1) A (2) B (3) C (4) D

24. ***Assertion :-*** Benzaldehyde with alkaline $CuSO_4$ gives red-brown precipitate.

Reason :- Red precipitate is due to Cu_2O.

(1) A (2) B (3) C (4) D

25. ***Assertion :-*** Methoxy ethane has more boiling point than propanal.

Reason :- Attraction is more in methoxy ethane than propanal.

(1) A (2) B (3) C (4) D

EXERCISE-II (Assertion & Reason) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**1**	**4**	**2**	**1**	**1**	**4**	**3**	**3**	**2**	**2**	**4**	**4**	**3**	**2**	**1**
Que.	16	17	18	19	20	21	22	23	24	25					
Ans.	**2**	**3**	**1**	**1**	**3**	**4**	**3**	**3**	**4**	**4**					